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16085 U.S. PTO

PTO/SB/16 (04-04)

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**PROVISIONAL APPLICATION FOR PATENT COVER SHEET**

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto					
TITLE OF THE INVENTION (500 characters max)					
AMPLIFICATION OF SINGLE WALL CARBON NANOTUBES					
Direct all correspondence to: CORRESPONDENCE ADDRESS					
<input type="checkbox"/> Customer Number: <div style="border: 1px solid black; width: 250px; height: 30px; display: inline-block;"></div>					
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[Page 1 of 2]

Respectfully submitted

Date August 4, 2004SIGNATURE Edward T. MickelsonREGISTRATION NO. 50,413

(if appropriate)

TYPED or PRINTED NAME Edward T. MickelsonDocket Number: 11321-P091V1TELEPHONE (713) 650-2632**USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT**

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**Docket Number** 11321-P091V1

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## SWNT AMPLIFIER DEMONSTRATION PROJECT

**Objective:** Demonstrate SWNT growth from catalyzed SWNT seeds (SWNTcat) and verify that newly grown SWNT has same (n,m) as the SWNT seeds from which they were grown.

Single walled carbon nanotubes (SWNT) are polymers of carbon uniquely specified by two indices (n,m). We have envisioned a new process to manufacture these polymers with complete control of (n,m). In this process the catalyst is a molecule (a "SWNTcat") which consists of a short length SWNT of the desired (n,m) chemically attached at one or both open ends to a transition metal cluster. When injected into a reactor this SWNTcat becomes activated for growth from a gas phase feed stock (e.g., carbon monoxide, methane, ethanol), the short SWNT piece acting as a seed for the growth of a perfect SWNT molecule many microns in length, all of the same, constant (n,m) value. A small fraction of the SWNT product from this process is then cut into short lengths to generate many more SWNTcat seeds and fed back as an input "signal" into the reactor. Overall the process we are envisioning is therefore, effectively, a SWNT amplifier. We anticipate that the gain of this amplifier could exceed 1000, with extremely high fidelity (the (n,m) distribution of the product faithfully following the (n,m) distribution of the input). We also anticipate that this SWNT amplifier process can be developed to operate on a scale of many tons per day at low cost.

We describe below a six-month research project to demonstrate the single most critical element of this SWNT amplifier: growth from SWNTcat seeds. We will pursue multiple independent research paths both for SWNTcat preparation and for SWNTcat growth to insure successful demonstration of growth from seeds

There is already abundant evidence that SWNT growth occurs with a nanometer-sized metal catalyst riding on the open end of the carbon tube. This is particularly evident in the existing gas phase SWNT production methods of laser-oven and HiPco, but it is also clear in the best quality CVD growth of SWNT on supports. Individual SWNT have been imaged by TEM, STM, and AFM techniques and are generally found to be straight, and of constant diameter for many microns. This is readily understandable since in order for the growing tube to switch to a different value of (n,m) there must be at least one pentagon defect and one heptagon defect incorporated into the hexagonal carbon lattice on opposite sides of the tube, causing the tube to bend abruptly and requiring an energy cost of at least 5 eV. At the 500-1200°C growth temperatures used in these methods the statistical likelihood of two such high-energy defects occurring simultaneously under equilibrium (reversible) growth conditions is negligible. So if growth is slow enough, defects will be annealed away before they result in (n,m)-changing pentagon/heptagon events frozen into the structure. Even if the metal catalyst particle attached to the growing end of the tube grows to be larger than the tube diameter itself (or shrinks by evaporation of some of the metal to be slightly smaller than the tube), the SWNT will continue to prefer growth with constant diameter and (n,m) value.

The issue here is not whether a metal catalyst particle *once docked to the open end of the SWNT* will cause the tube to grow with constant (n,m). We believe that is already well established. Our



challenge is, rather, to prove that we can get a metal particle to dock to the open end of a pre-existing SWNT, and activate this so that it catalyzes the growth of the SWNT as a living polymer and do this in a practical way that can lead to a large scale, low cost commercial process.

In order to do this it will be necessary to have the SWNTcat truly soluble in some solvent so that each SWNTcat molecule can be injected into a reactor and grow long with preservation of (n,m). Although there are other possible schemes, we will focus our efforts on SWNTcat composed of a short length of SWNT attached at the ends to a particular iron molybdate cluster we call FeMoC. This cluster contains 30 Fe(III) atoms and 72 Mo(VI) atoms bound to one another through intervening oxygen atoms in a giant geodesic cage, 2.3 nm in diameter. During this past year we (Barron, et al.) have developed an effective synthesis that renders this cluster highly soluble in ethanol. It is a robust, air stable molecule in ethanol solution and we expect the preparation may be scaled up to kilograms at low cost. We have also demonstrated that it can be linked to the carboxylic acid groups on the open ends of SWNT, and have begun some initial experiments casting these SWNT-FeMoC molecules on surfaces, and have successfully heated them to 700°C in a hydrogen atmosphere, demonstrating that the FeMoC does indeed remain docked to the open end of the SWNT and catalyzes the hydrogen etching of the SWNT. It is time now to demonstrate that the SWNT seed prepared in such a way can be activated for growth.

#### **Experimental Protocol:**

1. Prepare SWNTcat
  - a. make SWNT using existing techniques (HiPco)
  - b. cut SWNT to short pieces
  - c. solubilize SWNT
  - d. make catalyst precursor, FeMoC
  - e. tether FeMoC to open ends of SWNT to make SWNTcat
  - f. purify SWNTcat solution
2. Demonstrate growth of SWNT from SWNTcat
  - a. on flat surfaces (HOPG, MgO)
  - b. on powders (MgO)
  - c. in the gas phase
3. Verify SWNT growth is from seeds with preservation of (n,m)
  - a. AFM growth pattern analysis
  - b. Raman analysis
  - c. band-gap fluorescence analysis
  - d. SWNTcat sensitivity (response of growth process to different SWNT seed sets)

We include a “gas-phase” growth experiment because there are complications that we may encounter for growth of SWNTcat on surfaces that may take more than 6 months to work around. We anticipate three principal complications: (1) on weakly interacting supports such as HOPG (highly oriented pyrolytic graphite) the SWNTcat diffuse over the surface when they are

heated and congregate at the step edges, making it difficult to follow the growth history of individual tubes, (2) metal catalyst impurities from the SWNTcat preparation can diffuse to the SWNTcat, fattening the catalyst at the open ends to the point that it overcoats and deactivates under growth conditions, and (3) on strongly interacting supports such as silica, alumina, and possibly MgO as well, the SWNTcat-surface interaction may be too strong to permit the SWNT to grow freely. In the gas phase experiment we inject the ethanol solution of the SWNTcat directly into a heated growth gas, evaporate away the ethanol, and arrange that each SWNTcat has an opportunity to grow alone.

### **Success Criteria**

Amplification on surfaces will be proven by:

1. SWNT grow as direct, straight extensions of specific SWNT seeds
2. Grown SWNT have same Raman spectra as seeds
3. SWNT growth does not happen in absence of SWNTcat

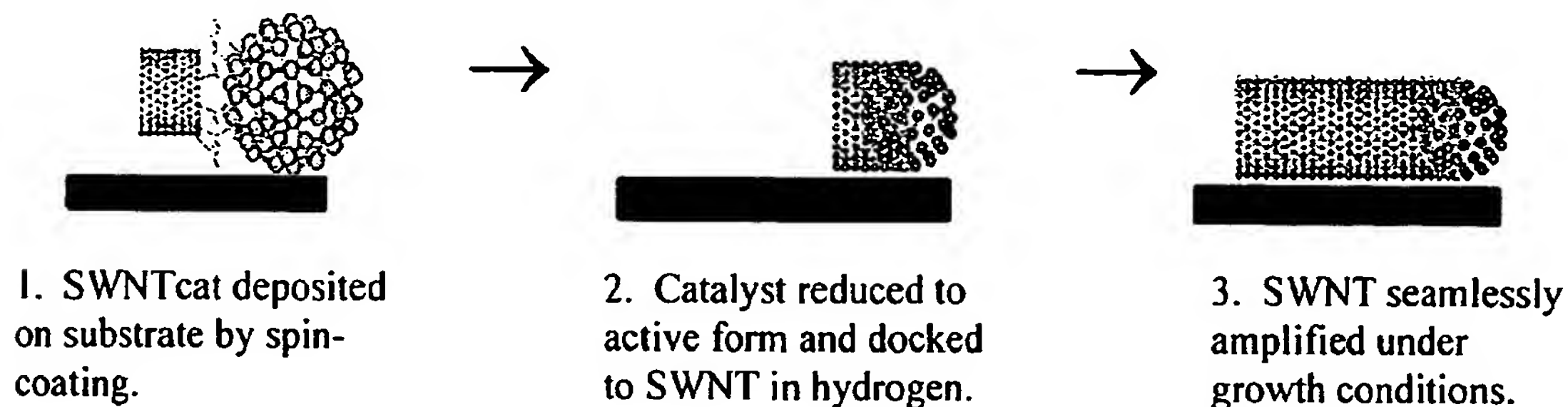
Amplification in the gas phase will be proven by:

1. Growth appreciably increases mass of and length of starting material
2. Grown SWNT have same direct band-gap fluorescence spectra as SWNT seeds
3. Grown SWNT have same Raman spectra as seeds
4. SWNT growth does not happen in absence of SWNTcat



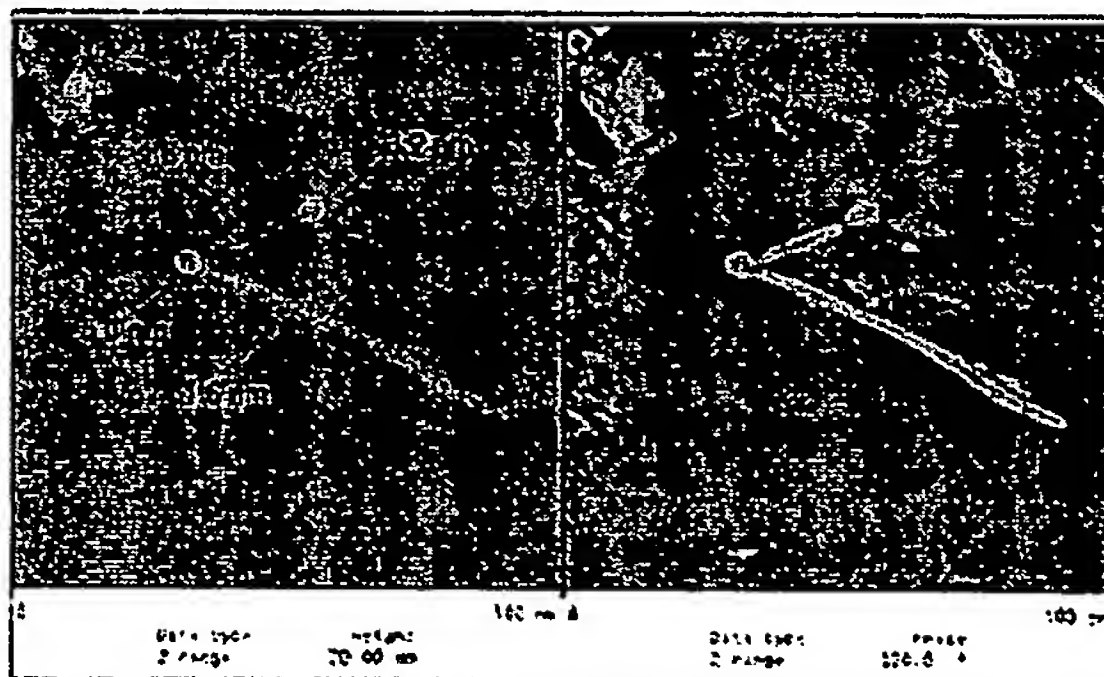
### Task 1: SWNTcat Growth on Surfaces (Smalley, Hauge)

The objective of this Task is to achieve and very clearly document SWNTcat growth on well-defined surfaces, as shown schematically below. Our approach includes AFM observations of step-wise process chemistry on *specific, individual* SWNTcat sparsely distributed on flat, ordered inert surfaces. A successful demonstration will uniquely separate SWNT nucleation and growth processes, and establish the first means for producing type-selected SWNT.



SWNTcat in solutions (e.g. chloroform, ethanol) can be spin coated onto various surfaces such as highly ordered pyrolytic graphite (HOPG), magnesium oxide (MgO), aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and silicon oxide ( $\text{SiO}_2$ ). Then the metal oxide catalyst will be reduced to metal in hydrogen and begin etching back the SWNT so that the catalyst and nanotube are in intimate contact. Then introduction of a growth gas will allow for the seamless growth of the SWNTcat.

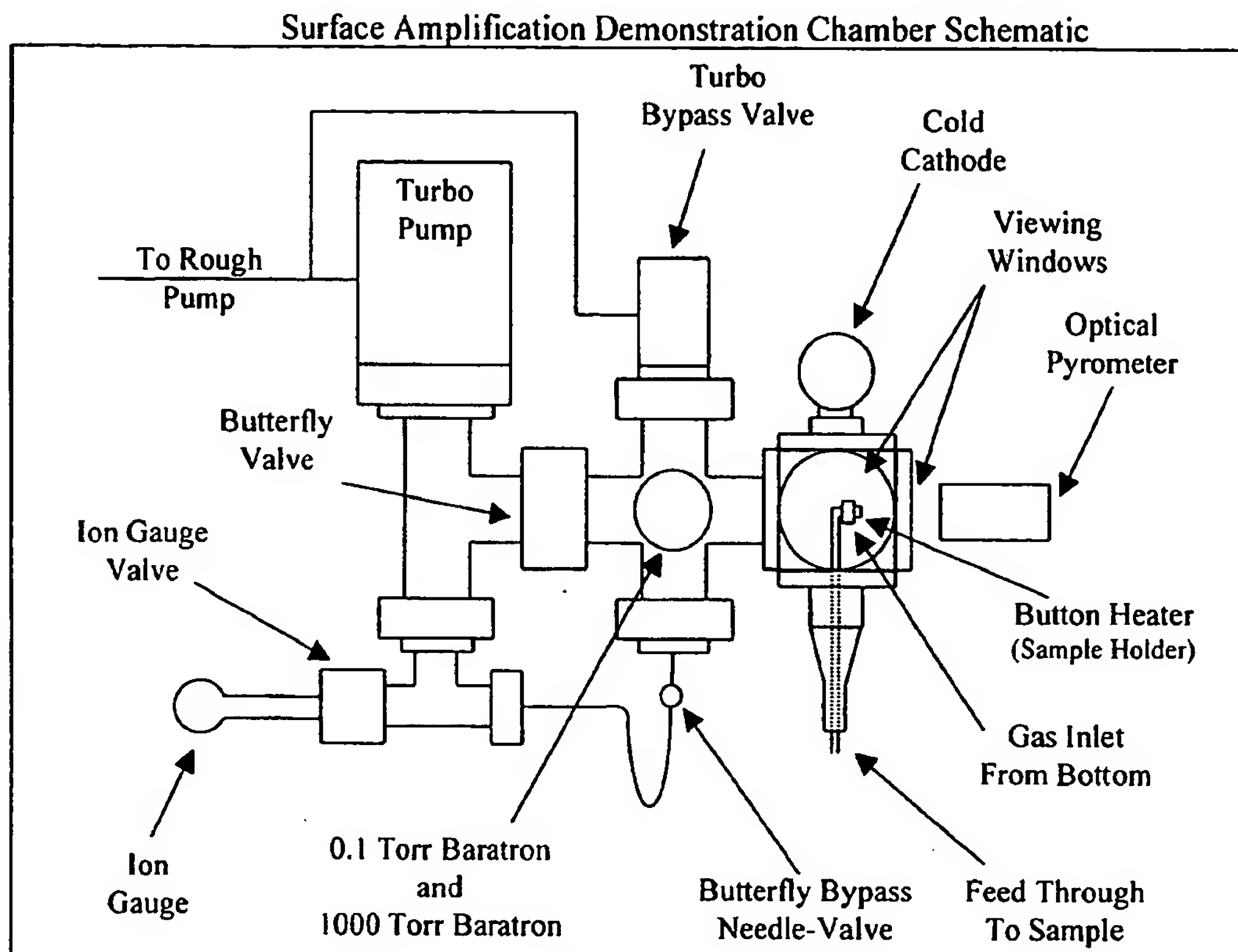
At right, for example, we show an AFM image, both in height and phase mode, from preliminary work using SWNTcat attached in chloroform; the SWNT are linear features about 1.5 nm high while the catalyst particles are round objects 3 to 5 nm in height. These SWNTcat were deposited from chloroform and imaged on HOPG. Process steps were attempted in a tube furnace.



The experimental apparatus, methods and materials described in the current Task are selected to resolve issues discovered previously:

- Stainless steel high vacuum-rated chamber replaces a tube furnace to reduce particulate contamination.
- Mass flow controllers replace rotameters to improve control and eliminate leaks.
- Explore MgO,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  substrates to gain more control over SWNTcat surface mobility.
- Ethanol based attachment replaces chloroform to improve attach-efficiency and eliminate metallic contaminants (Tasks 5, 6 and 7).

The system to be used in this work is shown the figure below. The high-vacuum chamber, gas manifold and pressure regulation components allow us to work at pressures ranging from atmosphere to  $10^{-6}$  Torr. A button heater is used to heat only the sample as high as  $1000^{\circ}\text{C}$  where surface temperature is monitored with an optical pyrometer.



The ability to reductively dock and grow is highly dependent on the interaction between the surface and SWNTcat. We have found that HOPG interacts least with the SWNTcat, rendering the entire SWNTcat mobile on the surface at elevated temperatures. In general, both SWNTcat and excess catalyst migrate to and accumulate at step edges on HOPG. Mobility should allow for facile reductive docking and growth but complicates our ability to monitor the same SWNTcat through each step.  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  interact more strongly with the SWNTcat making it easy to re-locate particular SWNTcat individuals, but immobility may hinder reductive docking and growth.

Our primary means for tracking step-wise changes (docking, reduction, and growth) and interactions between individual catalyst-SWNT pairs remains AFM. Ideally, we will observe a compelling number of specific SWNTcat that visibly shorten during reductive docking and then extend under growth conditions. This will provide visually simple and incontrovertible proof of growth from seeds – amplification – and all that it implies.

We shall continue to examine and document docking and growth primarily on step edges on HOPG in this Task. SWNTcat mobility is a complicating factor, but there is much to be learned from this apparently inert surface. Key factors for mitigating migration include operating at low



coverage (dilute SWNTcat solutions), eliminating unbound catalyst, and controlling SWNT-catalyst stoichiometry (Tasks 5, 6 & 7). We shall also explore controlling migration by introducing additional step-edges with a damage-etch cycle (plasma & oxidation processing) prior to introducing SWNTcat to the HOPG surface. When we see growth, we can confirm growth from seeds, SWNTcat, in several ways:

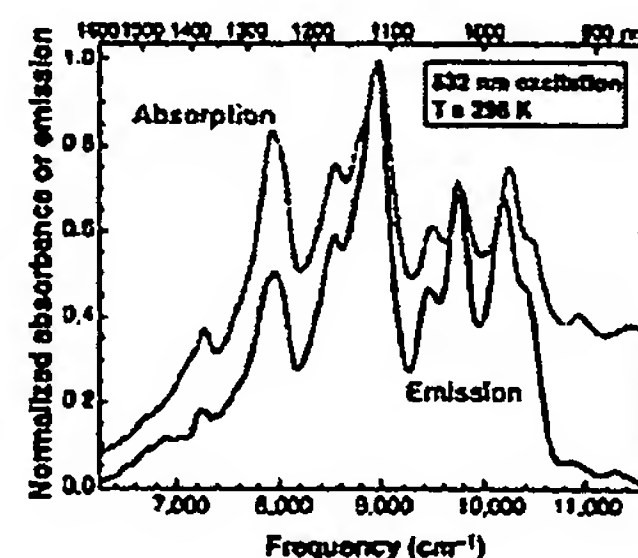
- Determine that no growth happens with FeMoC alone, or SWNT alone.
- Confirm that tubes smoothly conform to the step edge, with no height changes.
- Measure the growth rate as a function of temperature and gas composition – we expect some dependency on (n,m), *i.e.* armchairs differ from zigzags.
- Measure the etching rate in reductive docking as a function of temperature and gas composition (H<sub>2</sub> etching, compared to CO<sub>2</sub> etching). This should also depend on (n,m).
- Determine conditions that stop growth.
- Determine conditions that can reactivate growth.
- Determine conditions that support growth, imaging, etching back, imaging, and re-growth – all without kinks or changes in diameter or growth/etch rates.

We shall also explore SWNTcat amplification on other surfaces, primarily MgO, but also including Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>. MgO currently appears to be our best alternative to HOPG both because MgO appears to be the most weakly interacting of the oxide supports, and because it is actually the preferred substrate to use industrially. We may find that it is too strongly interacting, even so, in which case we will focus on extremely short SWNT, and SWNTcat that have catalyst (FeMoC) on one end only.

## Task 2: Gas Phase Amplification (Smalley, Schmidt, Hauge)

In this Task we shall pursue amplification using gas phase growth from SWNTcat generated from spectroscopically distinct SWNT feedstocks. This Task is motivated by the prudent realization that SWNTcat-surfaces interactions in Task 1 may complicate the demonstration in unforeseeable ways. Our approach utilizes SWNTcat solutions sprayed into a typical tube furnace reactor along with suitable feedstocks proven to support SWNT growth in the 600 to 1200 °C range. In particular, we anticipate electrospraying ethanolic SWNTcat to disperse individual seeds into a growth medium of hydrogen and ethanol vapor between 600 and 800°C will achieve growth from the seeds.

The relative abundance of the many different semiconducting nanotubes in a given SWNT sample is readily determined by near infra-red fluorescence (NIRF) and absorption spectroscopy (figure at right) [M. J. O'Connell, et al., Science 297 (2002) 593]. Different SWNT production methods (*e.g.* HiPco, laser-oven, arcs) produce different and distinct mixtures of nanotube types. Furthermore, small diameter tubes can be selectively removed from a given population by digestion in a sulfuric and nitric acid mixture or with piranha.



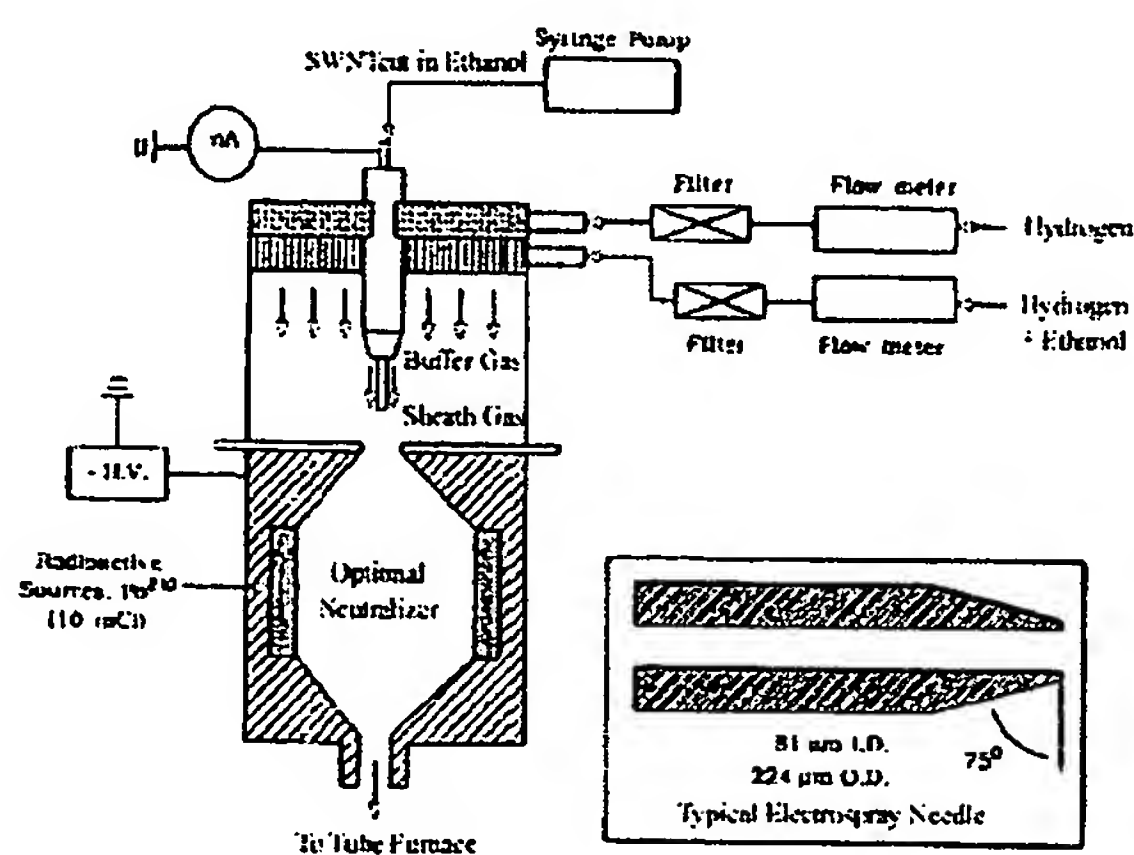
We shall collect NIRF 'fingerprint' spectra from our SWNTcat starting material and the output from the reactor. Since growth systems normally show some preference for some tube types over others, we can reasonably expect that not every tube in the starting material will be amplified at the same rate. Thus, amplification of the starting SWNTcat will be demonstrated if no new features (nanotube types) appear in the final product. An internal control will be obtained by spraying FeMoC (without SWNT seeds) into the reactor at temperatures high enough (typically over 900°C) to support independent nucleation of new nanotubes. We shall select or produce SWNTcat feedstock lacking at least one spectral feature that is prominent in the internal control.

Several spraying techniques are available, including ultrasonic sprayers, fast-flow nebulizers and electrospray. Since we ideally want to completely isolate individual SWNTcat, or at least obtain very small bundles of no more than about ten SWNTcat, small droplet size is essential, and leads us to focus on electrospray [d. Chen, et al., J. Aerosol Sci., 26 (1995) 963]. Highly charged initial droplets in the 100 nm range undergo 'coulomb explosion' until individual ions remain (figure at right). This method is routinely employed in commercial mass spectrometers for spraying undamaged and individual biomolecules up to the megaDalton range. Electrospray Ionization-Mass Spectrometry (ESI-MS) of organics (similar to SWNT) is routine, and ESI-MS of polymolybdates (similar to FeMoC) [D. K. Walanda, et al., J. Chem. Soc., Dalton Trans., (1999) 311] and organic sulfonates [T. Keough, et al., Anal. Chem., April 1, 2003, 166A] have been reported without difficulty, so we can reasonably expect success with our materials.



Schematic of typical electrospray source.

Electrosprayed organo-metallic precursors have been introduced into tube furnaces to effectively generate ZnS nanoparticle aerosols [I. W. Lenggoro, et al., J. Aerosol Sci. 31 (2000) 121]. In this case, a downstream neutralizer was employed to arrest coulomb explosion and reduce product losses to walls and counter-electrodes. We shall include a neutralizer option and roughly determine conditions for simultaneously optimizing dispersion, growth and throughput. The schematic at right shows a SWNTcat electrospray source in the basic amplifier, Configuration I.



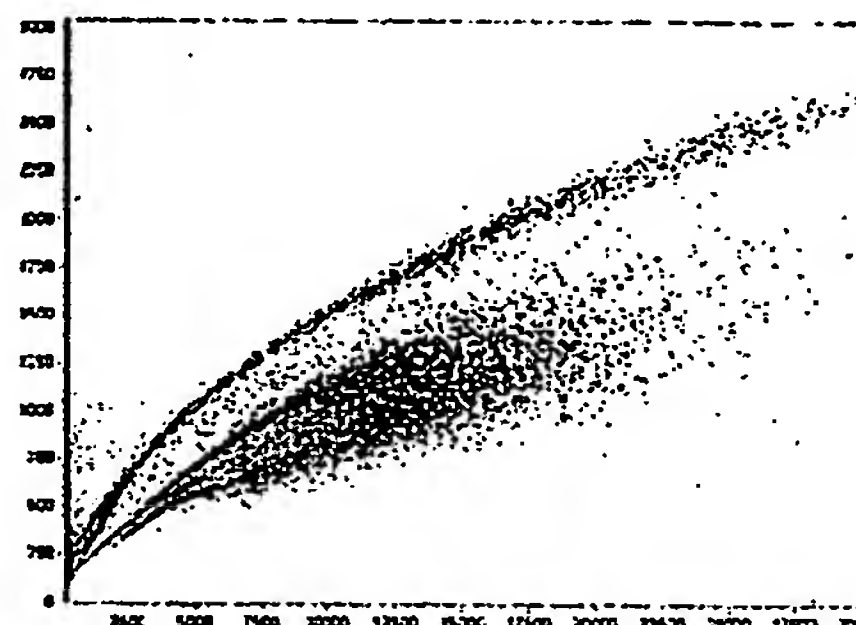
Of the several SWNT growth chemistries available, we expect to utilize the hydrogen + alcohol system for compatibility with the SWNTcat solvent. Calculations show, however, that the amount of ethanol to be electrosprayed would not significantly dilute the CO feedstock in a HiPco system.



In this demonstration study we intend to operate a single electrospray source under standard conditions, streaming the dispersed seeds into a 2" tube furnace reactor. We shall survey three basic injection configurations, initially constructing and evaluating Configuration I, and implementing the others if the analytical results are compelling and time allows:

- I. Spray and neutralize seeds into carrier gas entering the reactor.
- II. Spray seeds into a pre-heated (& neutralizing) gas stream, and
- III. Electrically drive ionized seeds rapidly into the reactor's hot zone.

We expect to use a 0.1 weight percent solution of 50nm SWNTcat in ethanol. With a very nominal supply rate of 1 nanoliter per minute, the source should generate about  $1.67 \times 10^{11}$  dispersed seeds per second. With a carrier gas supply rate of one SLM, the resulting gas phase density of seeds will be roughly  $10^{10} \text{ cm}^{-3}$ . If left as singly-charged ions, this swarm will generate by space-charge a surface field of about 100 volts/cm.



Extrapolating from preliminary data on ion mobility of short nanotubes, we can estimate the resulting expansion velocity to be about 15 cm per second. Thus, we can neutralize the ion cloud using a  $^{210}\text{Po}$  or  $^{241}\text{Am}$  alpha source within a few cm of the electrospray needle and maintain a high concentration of disperse SWNTcat.

From the above Ion Mobility (vertical axis) versus Mass Spectrum (horizontal) of cut nanotubes, we can estimate the expansion rate of SWNTcat due to space charge. [Unpublished work by Hauge (Rice/CNL) and Schultz (Ionwerks)].

In configuration I, the neutralized seeds flow into the reactor for amplification. At 1 SLM, the velocity of the carrier gas will be about 1.2 cm per second through the tube furnace. Once SWNTcat are neutralized we will have to be concerned with their self-aggregation; at the initial density, we estimate their collision rate at 10 per second, at the most. Therefore, we can expect that in this configuration most of the SWNTcat will enter the furnace as very small bundles of 10 to 30 seeds; we expect that these will grow and amplify adequately. While we are concerned about bungling impeding growth, we also believe that bundling effects may be mitigated in our favor by ablative departure of sidewall functionalization as the SWNTcat heat beyond 400 °C. Similarly, we are confident that aggregating catalyst particles up to a few nm in diameter will still support SWNT growth without over-coating or nucleating new nanotubes.

Configuration II will defeat aggregation prior to growth by spraying into a small gap between a pair of hot zones. Configuration III will defeat aggregation and accelerate heating by drawing charged seeds toward a counter electrode maintained in the hot zone of the reactor [D. E. Clemmer, et al., J. Mass Spec. 32 (1997) 255]. In cases I and II, product will be collected from a filter downstream of the reactor. In case III, product will be recovered from the surface of the hot electrode.

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We estimate that any of these configurations will produce between 1 and 10 mg of nanotube material per hour, more than sufficient for spectroscopic characterization and demonstration of the SWNT amplifier. We anticipate that this approach is scalable through developing higher volume spray conditions, exploiting ablative functionalization and implementing arrayed sources.

### Task 3: SWNT Preparation & Tuning (Smalley, Hauge)

The starting material optimized for SWNTcat Amplifier research (high purity, tuned diameter and type) will come from the Rice/CNL HiPco reactor in this Task effort. We shall explore nucleation, growth, purification, and post-treatment conditions to prepare SWNT with distinct diameter and type distributions to use as distinct "signals" for the SWNT amplifier. Particular care will be given to purification to eliminate adventitious iron in SWNTcat preparation and amplification.

This reactor currently produces SWNT at the rate of ~1gram/hour, sufficient for project needs. The chirality distribution under typical operating conditions has been documented with SWNT fluorescence and Raman spectroscopy. Typically the number of tube types is more than 20, predominantly armchair or near-armchair types. The average tube diameter is ~0.95 nm and average length about one micron.

#### Tuning the type-distribution

We have recently shown that by reducing the metal catalyst concentration that the average SWNT length increases dramatically, and the type-distribution shifts somewhat. Thus, we shall explore the extremes of catalyst-rich and catalyst-starved conditions to shift average tube diameter. We shall also explore the effect of several additives to shift catalyst nucleation chemistry, including H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and thiophene; we expect that these could shift the armchair-zigzag ratio of the final product. SWNT materials will be characterized with Raman, UV-Visible absorption and Near Infra-Red Fluorescence prior to delivery to the other Tasks in this Project.

Our prior tuning studies on the HiPco reactor have also shown that less than one in a thousand of the iron atoms that are inserted participate in growing nanotubes. This serves to emphasize the importance of the future development of direct insertion of SWNTcat as individuals into a HiPco-like reactor where every SWNTcat is likely to produce a nanotube. Operation of a HiPco-like apparatus in this manner will increase the production of SWNT and decrease the concentration of residual catalyst and other forms of carbon in the SWNT by an estimated two orders of magnitude. Most importantly, the SWNT will have the same chirality as the SWNTcat seeds.

### Task 4: SWNT cutting (Smalley, Hauge)

This Task will deliver gram-scale quantities of well-characterized short SWNT to the functionalization and SWNTcat preparation Tasks. SWNT cutting on a milligram scale with sonication in a mixture of conc. sulfuric acid and nitric (3/1) at 40°C has been shown to cut nanotubes to lengths from 100-300 nm. Subsequent etching at 70°C without sonication produces



nanotubes with lengths less than 100 nm. Nanotubes with lengths of roughly 100 nm will be used for our demonstration of SWNTcat growth on flat surfaces. Lengths of the order of 100 nm are necessary since the lowest measurable length with AFM is of the order of 20 nm due to the radius of commercially available silicon tips. However, we will need SWNTcat with lengths of 10-20 nm for the SWNT amplifier. This requires that we improve our current cutting process and/or develop new cutting methods that can eventually provide pounds of nanotubes cut to 10-20 nm.

The strategy for cutting is to randomly introduce SWNT sidewall carbon bond oxidation and damage by methods that can be scaled to pound quantities. This will be followed by chemical attack at the sidewall in an oxidizing environment. We have found that “piranha,” sulfuric acid with hydrogen peroxide, at room temperature effectively cuts at damage sites without rapid etch back of SWNT. Cutting in concentrated sulfuric acid or oleum (fuming sulfuric acid, i.e.  $\text{H}_2\text{SO}_4$  with dissolved  $\text{SO}_3$ ) is very effective because sulfuric acid readily intercalates in SWNT thereby transporting persulfate-oxidizing species to all damage sites. Although cutting to 10-20 nm is not necessary for our six-month objectives it is essential that research on the development of scalable cutting methods is started so that the time required for development of a SWNT amplifier is minimized once successful demonstration of SWNTcat growth is demonstrated.

Three approaches to sidewall oxidation and damage will be investigated, as follows; all materials will be characterized with Raman, UV-Visible absorption, Near Infra-Red Fluorescence and length distribution prior to delivery to other Tasks:

1. Three MeV e-beam irradiation of SWNT that has been sidewall fluorinated to a stoichiometry of  $\text{C}_2\text{F}$  is expected to yield a random distribution of sidewall damage sites where carbon bonds have been broken. The electrons cause extensive local energy deposition primarily through local ionization that should result in carbon bond rearrangement with formation of carbon edges that are fluorinated. High-energy electron beams easily penetrate centimeters in carbon samples thus permitting uniform activation of large amounts of sample. Electron irradiation will be carried out at the AFML electron beam facility in Dayton Ohio. The  $\text{C}_2\text{F}$  SWNT will be reduced to SWNT and cut with piranha. SWNT length distributions will be measured with AFM. However, for SWNT with lengths less than 20 nm new measurement methods are needed. Cryo TEM and/or staining of SWNT supported on thin carbon films are promising methods for short length measurements.
2. Direct ozonation of SWNT dispersed in a fluorocarbon fluid leads to extensive oxidation of SWNT. Oxidation occurs for all SWNT throughout the sample when exposed to ozone. Weight increases of the order of 10 % are observed. The product of ozonation is most likely clustered surface epoxy groups since addition of an initial surface oxygen activates near by carbon atoms for oxygen addition. Clusters of oxygen epoxy sites are thought to be necessary for subsequent carbon bond breaking steps that lead to carbon loss as carboxylic acids and subsequent cutting at cluster sites. Activation of cutting will be carried out in piranha.
3. Many studies have demonstrated cutting of SWNT in sulfuric/nitric acid. However, rapid etching of the cut SWNT can occur. In addition one often obtains oxidized

carbon fragments that adhere to the remaining SWNT and are difficult to remove. We propose instead to disperse SWNT in oleum at elevated temperature with only sufficient nitric acid to create clusters of oxidized surface sites. This mixture will be cooled to room temperature where persulfate is added to create a piranha environment. Oleum is an excellent medium in which to oxidize SWNT since it transports oxidizers to all SWNT surfaces.

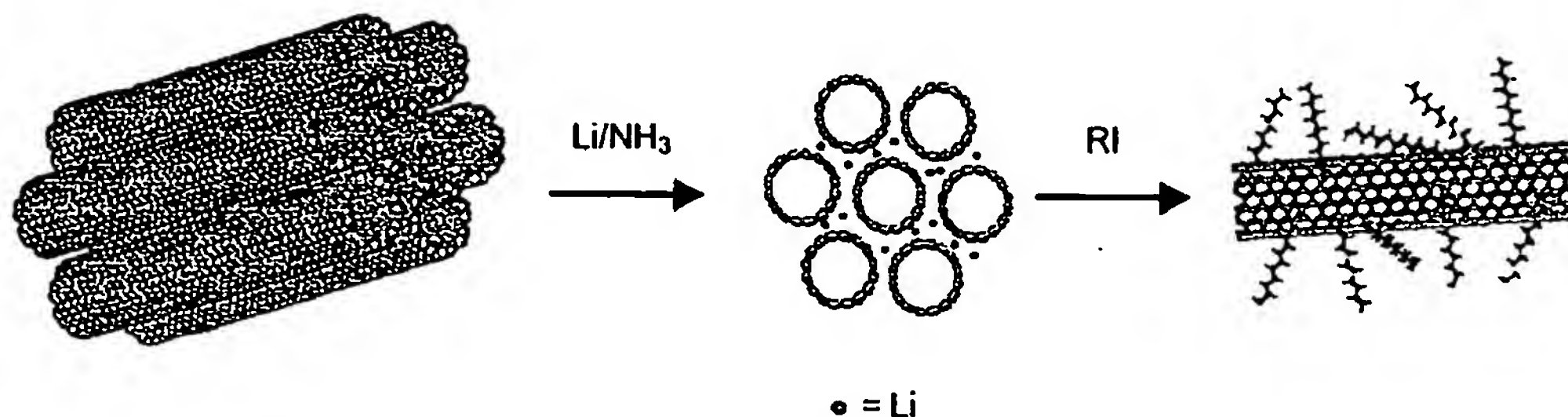
#### Task 5: SWNT solubilization via Birch Alkylation (Billups)

Along with Task 6, the goal of this Task is to deliver 100 mg quantities of ethanol-soluble, functionalized SWNT to Task 7. We pursue two parallel paths for this critical protocol step to ensure successful completion in a timely manner. True solubilization of SWNT in polar solvents such as alcohols and water is required for high volume production of SWNTcat where nanometer sized metal catalysts are attached to the ends of cut SWNT. It is important that the SWNT solutions are thermodynamically stable as opposed to, for example, surfactant stabilized SWNT dispersions in water. The problem with surfactant stabilization is that large excess concentrations of surfactant are necessary for stable suspension. It is however clear that the charged end groups present in cationic and anionic surfactants are very important to dispersion in polar solvents.

Our approach to achieving stable solutions of SWNT in polar solvents is to covalently attach surfactant-like groups to the sidewalls of SWNT. This provides for the attachment of highly hydrophilic groups without the need for excess surfactant-like species. Fortunately the Billups and Tour research groups at Rice have recently developed two very general scaleable methods for extensive sidewall functionalization of SWNT. We will use these methods to covalently bind surfactant-like surface groups. Two groups of particular interest are the p-phenylsulfonic anion and p-phenylalkyl quaternary ammonium cation, groups that are widely used in anionic and cationic surfactants. Other groups of interest are covalently bound polyethylene oxides, polyvinyl alcohols and sugars for solubility in alcohol and alcohol/water solvents. The t-butyl phenyl as well as octyl groups have also been shown to provide solubility of SWNT in chloroform. The following discussion provides a description of the Billups and Tour chemical methods for sidewall functionalization of SWNT.

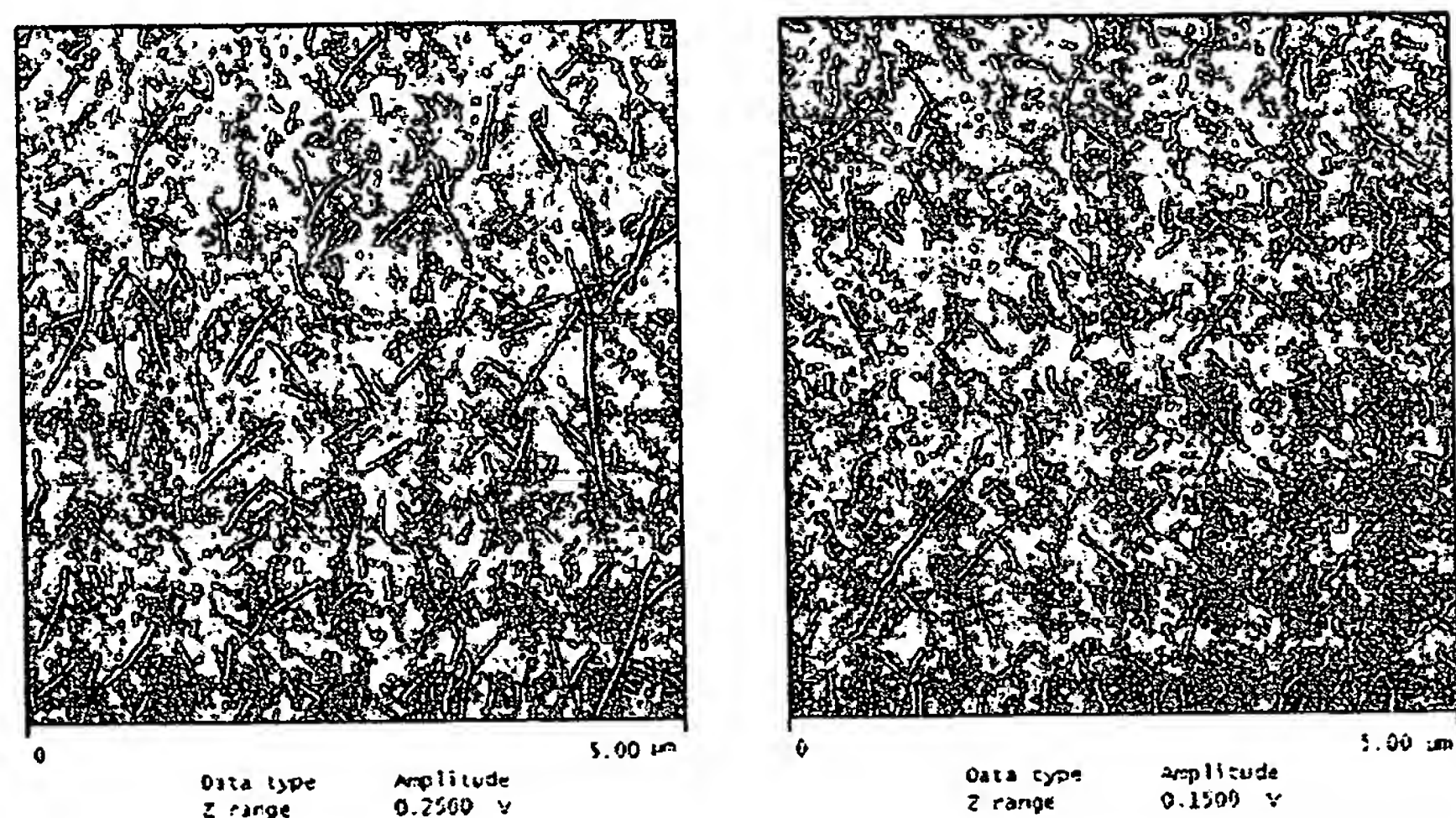
The Billups chemistry exploits a route to functionalized carbon nanotubes that involves reductive alkylation or arylation using lithium and alkyl or aryl halides in liquid ammonia. The reaction was discovered only recently (*Nano Letters*; web release date: 3-June-2004) and is outlined below. Preliminary experiments have demonstrated that this reaction leads to extensive debundling without sonication. The debundling is attributed to intercalation of lithium into the SWNT bundles.

The method is scalable and provides a route to SWNT that can be functionalized by a diversity



of groups. Studies have been carried out using both crude and purified SWNT (~1 wt % iron). The efficacy of this new reaction can be demonstrated by the following results using *n*-dodecylated SWNT. This material exhibits reasonably high solubility in chloroform, THF and DMF. Atomic force microscopy (AFM) images, recorded in chloroform, of the *n*-dodecylated SWNT prepared from purified (left) and raw SWNT (right) are presented on the following page.

The average diameter of the *n*-dodecylated nanotubes obtained from purified SWNT is around 2 nm as determined by their height, demonstrating that debundling has occurred. The diameter of the dodecylated nanotubes obtained from raw HiPco SWNT average only 1.5 nm, which is indicative of complete debundling. The “dots” that are visible in the AFM image from the raw SWNTS are 4-5 nm in height suggesting that they arise from the carbon encapsulated metal catalyst while the dots that have heights around 1.5 nm may belong to large fullerenes or very short tubes. The more extensive debundling that is observed when raw SWNT are used suggests that the purification process enhances bundling and thus debundling becomes more difficult.



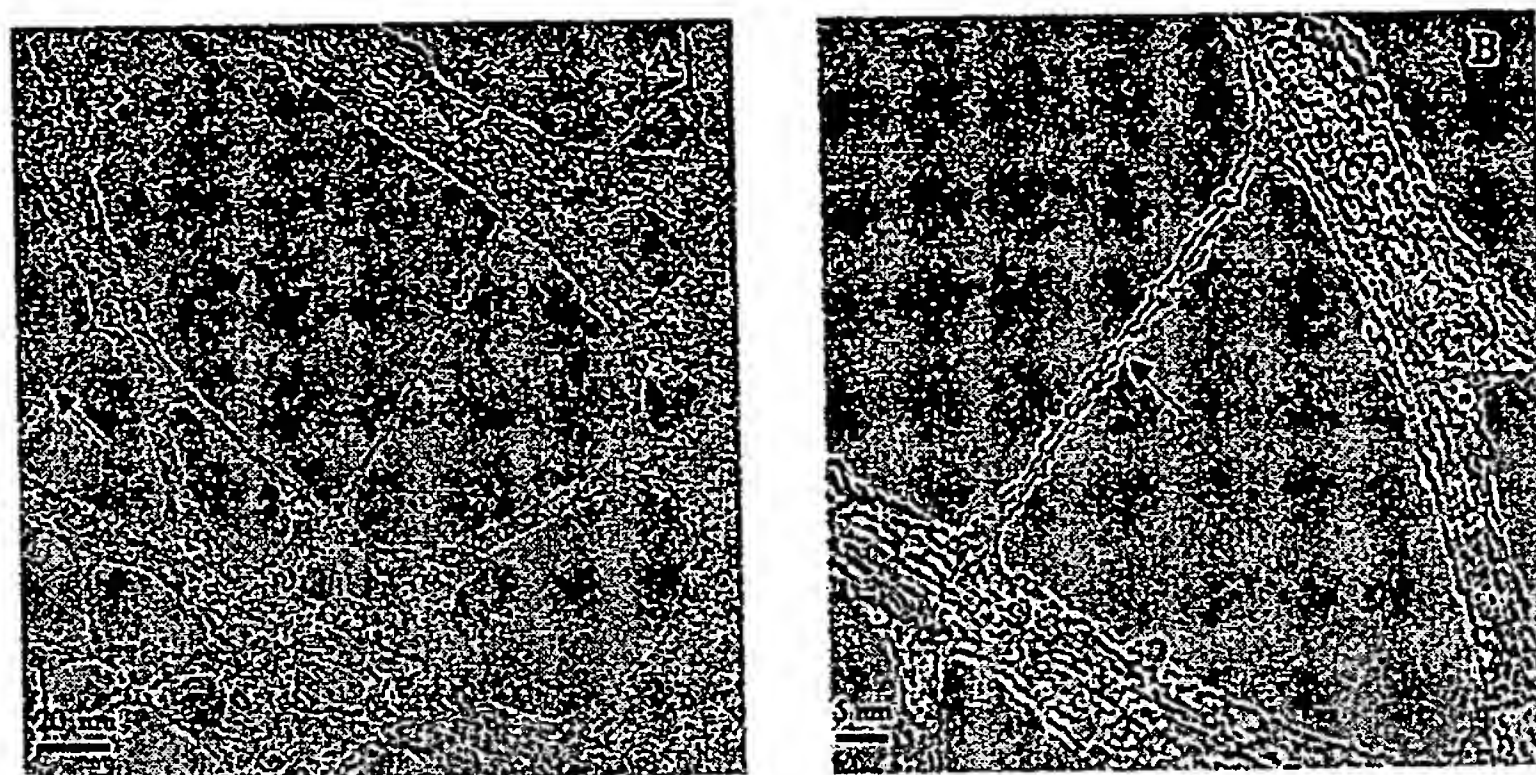
Tapping mode AFM Images of Dodecylated Purified SWNT (left) and Raw HiPco (right) Spin-coated onto Mica from Chloroform

Additional evidence for debundling is provided by inspection of the TEM images shown on the following page. The functionalized tubes exhibit a morphology that can be attributed to functionalization by the *n*-dodecyl groups. The debundling can be explained in terms of extensive intercalation by lithium leading to lithium ions dispersed between the negatively charged tubes. The intense blue color associated with solvated electrons disappears rapidly as the lithium is added to the suspension of nanotubes in liquid ammonia, suggesting that electron transfer to the SWNT is a facile process. Addition of the alkyl halide would lead to the formation of a radical anion that would dissociate readily to yield halide and the alkyl radical. It is well established that radicals add readily to nanotubes. A GC-MS analysis of the filtrate provides confirmation of the radical pathway. Thus *n*-C<sub>12</sub>H<sub>26</sub>, C<sub>12</sub>H<sub>24</sub> and *n*-C<sub>24</sub>H<sub>50</sub> are formed as by-products when *n*-dodecyl iodide is used as the alkylating reagent. *n*-C<sub>12</sub>H<sub>26</sub> and C<sub>12</sub>H<sub>24</sub> would arise from disproportionation of the dodecyl radicals whereas *n*-C<sub>24</sub>H<sub>50</sub> is formed by dimerization



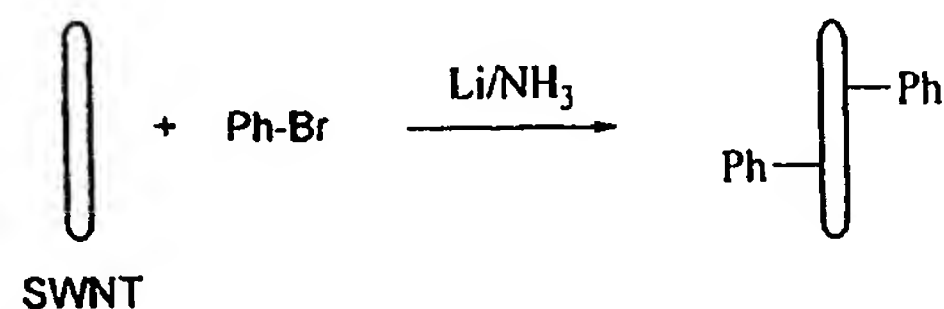
of dodecyl radicals. This inefficiency can be minimized by carefully controlling the stoichiometry.

Electron transfer to the nanotubes could be followed in liquid ammonia by Raman spectroscopy using a specially constructed apparatus. Eklund has previously studied doping of nanotubes by lithium and followed the process by Raman spectroscopy [Rao, A. M.; Eklund, P. C.; Bando, S.; Thess, A.; Smalley, R. E. *Nature*, 1997, 388, 257-259]. The blue color was observed to disappear as the lithium was added to a suspension of the SWNT in ammonia. The G-peak was observed to shift to lower frequency with a concomitant decrease in intensity. The reduction of the intensity is probably due to flooding of the conduction band with electrons. The blue color reemerged as more lithium was added suggesting that the nanotubes were "saturated" with electrons. In this way it was possible to determine that the carbon/lithium ratio was about 2.2.

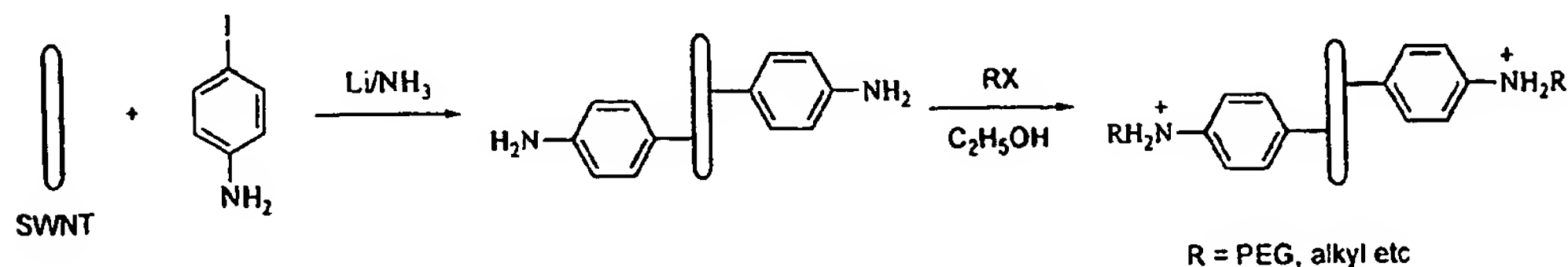


(A,B) TEM images of dodecylated SWNT

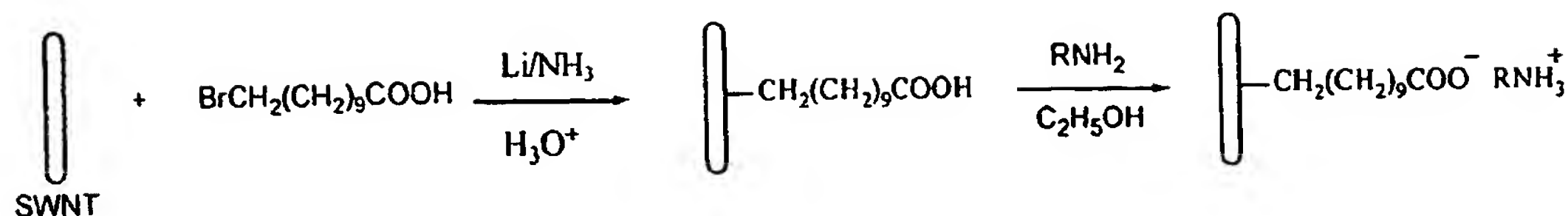
Addition of aryl groups via diazonium ions has played an important role in SWNT functionalization (Tour, Smalley et.al). Preliminary results indicate that aryl iodides also react readily with the lithiated SWNT as illustrated by the phenylation reaction using bromobenzene.



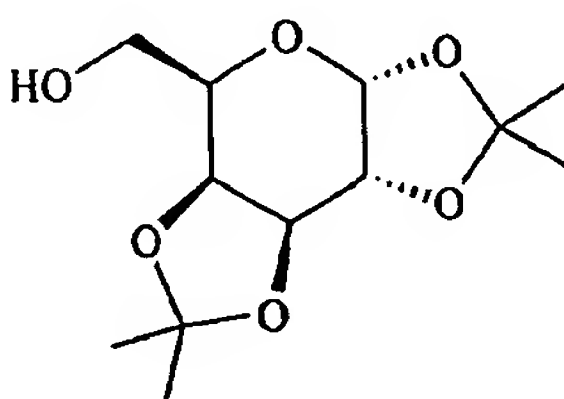
Similarly, 4-iodoaniline gives SWNT functionalized by aniline. This material can then be reacted with various halides in ethanol to give soluble ammonium salts.



A similar approach utilizes SWNT functionalized by carboxylic acids. Addition of an alkyl amine would yield soluble salts.



Sugars may also be attached. 1,2:3,4-Di-O-isopropylidene-D-galactopyranose is commercially available. Conversion to the bromide followed by sidewall attachment and removal of acetone will expose the sugar.



#### Task 6: SWNT Solubilization via Diazo Arylation in Oleum (Tour)

Along with Task 5, the goal of this Task is to deliver 100 mg quantities of ethanol-soluble, functionalized SWNT to Task 7. We pursue two parallel paths for this critical protocol step to ensure successful completion in a timely manner. The Tour chemical approach to SWNT sidewall functionalization is carried out in super acid media, as described in this section.

SWNT are promising building blocks for high performance composite materials.<sup>1</sup> An obstacle to fully exploiting the materials properties of SWNT is their tendency to spontaneously form bundles and/or flocculate in their unfunctionalized state due to the extraordinary 0.5 eV/nm intermolecular cohesive interaction between neighboring SWNTs.<sup>2</sup> Several methods have been used to functionalize SWNT bundles,<sup>2</sup> however, they generally do not exfoliate the bundles to produce individually functionalized nanotubes. We recently disclosed an exception<sup>3</sup> where individually functionalized SWNT could be obtained; however, yields of only ca. 15 mg of material could be obtained in 12 h. It has recently been reported that SWNT disperse as individuals and swollen ropes in superacids with SWNT concentrations of up to 10 wt %.<sup>4</sup>

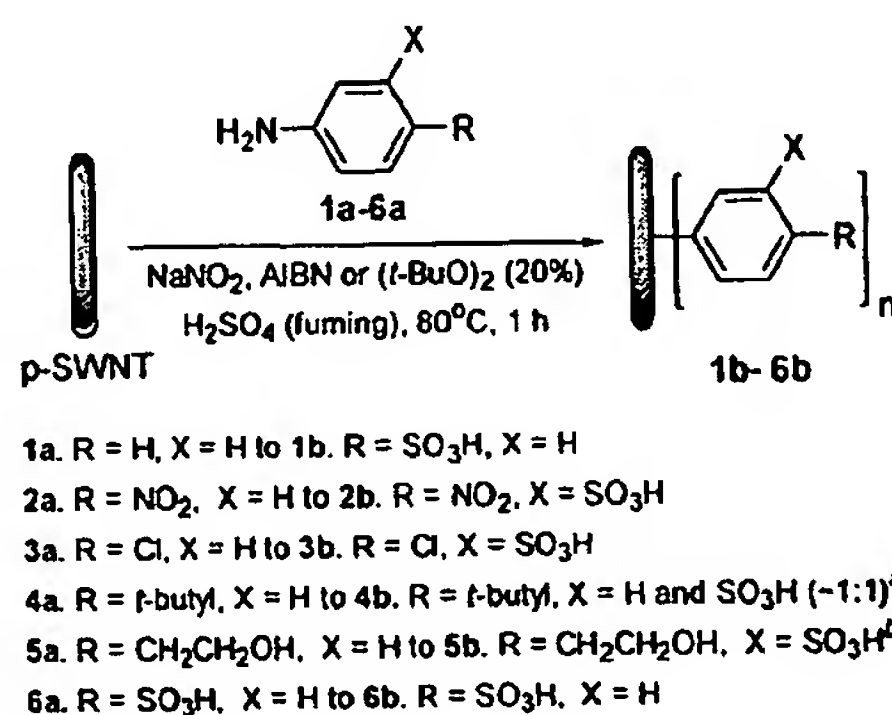


Figure 1. Functionalization of SWNT dispersed in oleum. XPS was used to determine the relative amount of sulfonation relative to the easily observed nitro- and chloro-moieties in 2b and 3b, and this was further correlated with the XPS data of the other products to show that in all cases, except 4b, there was approximately one  $\text{SO}_3\text{H}$  group per aryl addend. <sup>a</sup> The  $\text{SO}_3\text{H}$  regiochemistry (2- or 3-position relative to the nanotube) is not known and alkyl migrations are possible. <sup>b</sup> Cyclization to the 6-membered sulfonic ester is presumed to ensue.

Exploiting the solubility of SWNT and expansion of ropes in oleum, ( $\text{H}_2\text{SO}_4$ , 20% free  $\text{SO}_3$ ), we have modified the diazonium functionalization chemistry<sup>5</sup> to produce efficient functionalizations of nanotubes in that solvent. The aryl rings sulfonate under the reaction conditions thereby imparting the unusual water and alcohol

solubility to the final compounds (Figure 1). For example, the solid **3b** could be dispersed as individuals (unroped) in a variety of solvents including water, DMF, and EtOH (0.24, 0.16, and 0.06 mg mL<sup>-1</sup>, respectively).

The presence of individual SWNT was confirmed via atomic force microscopy (AFM) (tapping mode) by collecting height and phase data for numerous experimental products and controls. Figure 2a is an image of an individual SWNT sample of **3b**. The height, and thus diameter, of the tube ranges from 7-10 Å, with a mean diameter of 8 Å; this is consistent with the diameters of typical HiPco-produced tubes<sup>6</sup> but with small perturbations due to addend-based surface roughening.<sup>7</sup> Individual SWNT were the dominant feature in over 90% of the cases, but small bundles, typically 2-3 nm in diameter, were also observed.

Finally, transmission electron microscopy (TEM) revealed the presence of unbundled (throughout their entire length) surface roughened functionalized SWNT (Figure 3).<sup>5</sup>

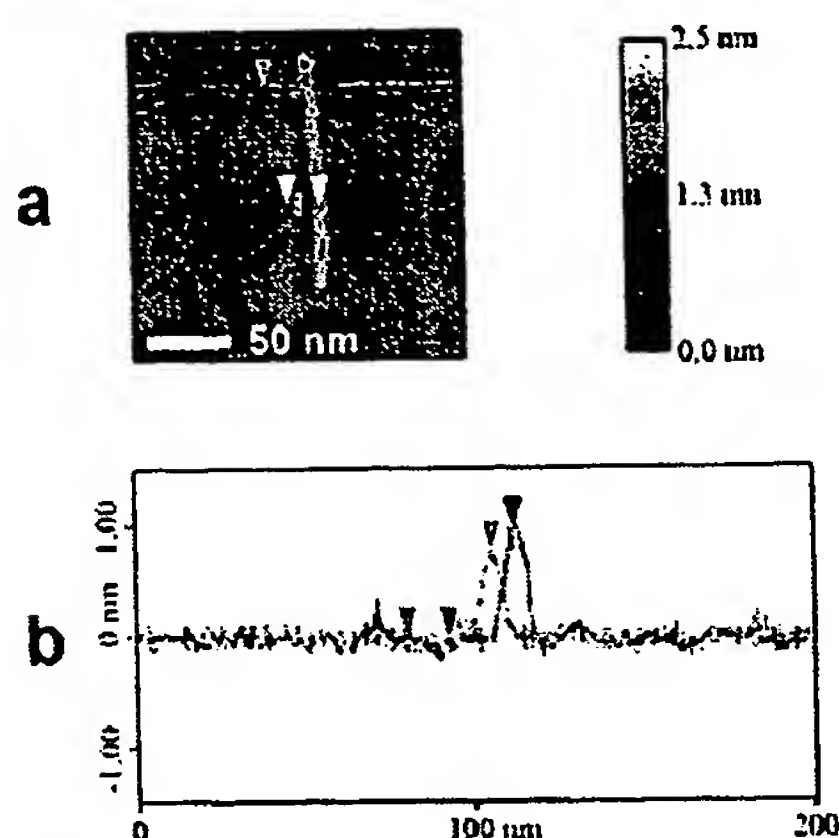


Figure 2. AFM analysis of **3b**. Section analysis of an individual 140-nm-long SWNT performed at (a) a low spot and high spot, and (b) the resulting cross-sections which show heights of 8 Å and 10 Å.

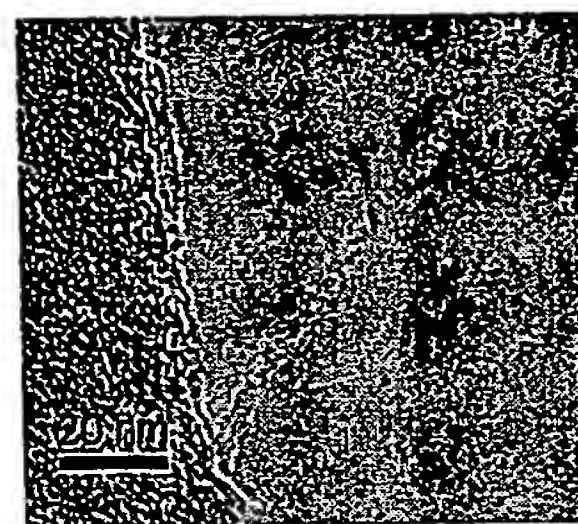


Figure 3. TEM of **3b** suspended from the lacy carbon TEM grid (20 nm bar).

### Functionalization of SDS-Wrapped Nanotubes

In cases where alcohol solubility is not critical and we merely seek to carry out some demonstrations of seeded growth on a surface, we have devised methods to cleanly generate individualized tubes by first surfactant wrapping, then using diazonium chemistry to permit the formation of addends to the SWNTs.<sup>3c</sup> We have recently demonstrated the individual functionalization reaction by reacting HiPco-produced SWNT that were wrapped in sodium dodecylsulfate (SDS). The starting suspensions were generated according to the published procedure by sonicating raw material in SDS then centrifuging to sediment the more dense bundles. Decanting the upper 75% of the supernatant gives suspensions, which predominately consist of less dense individualized SWNT. Functionalization of these stable suspensions of SDS-wrapped SWNT with diazonium salts gives heavily functionalized material with greatly increased solubility (Figure 4). Interestingly, this material disperses as individuals in organic solvent after removal of the surfactant (Figures 5 and 6).



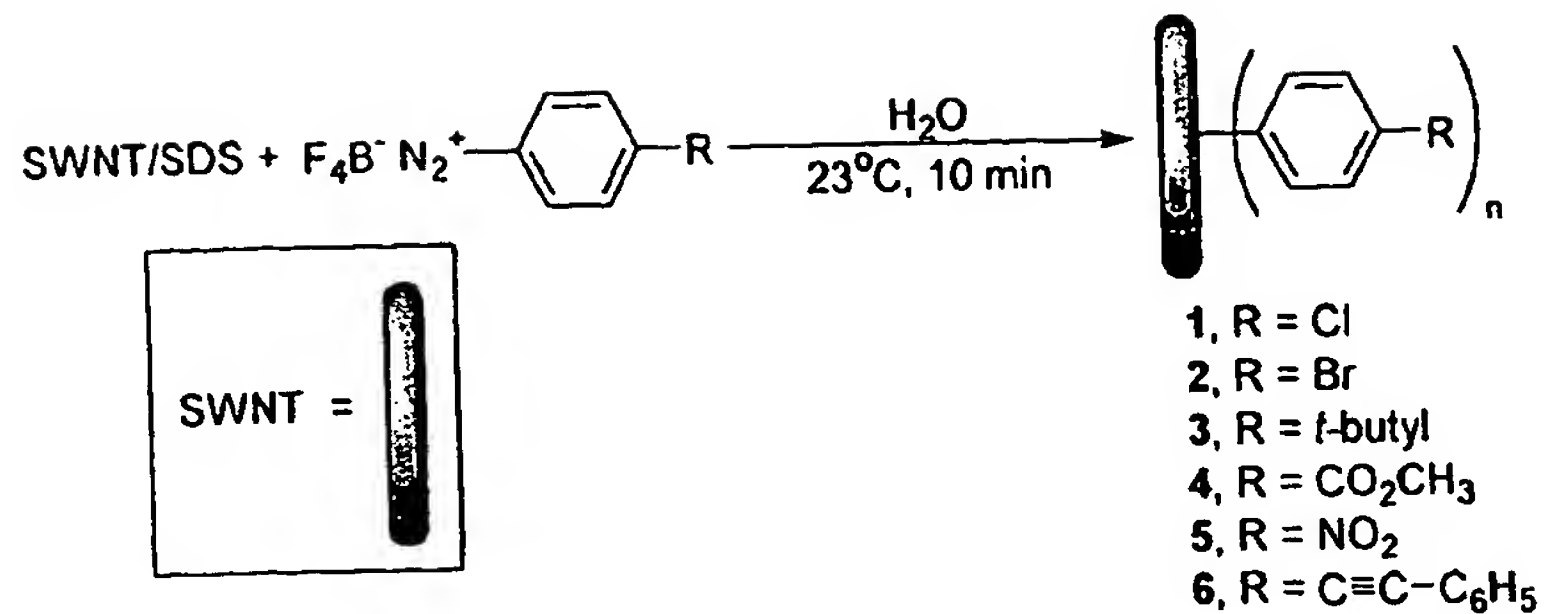


Figure 4. Functionalization of SWNT Coated with SDS.

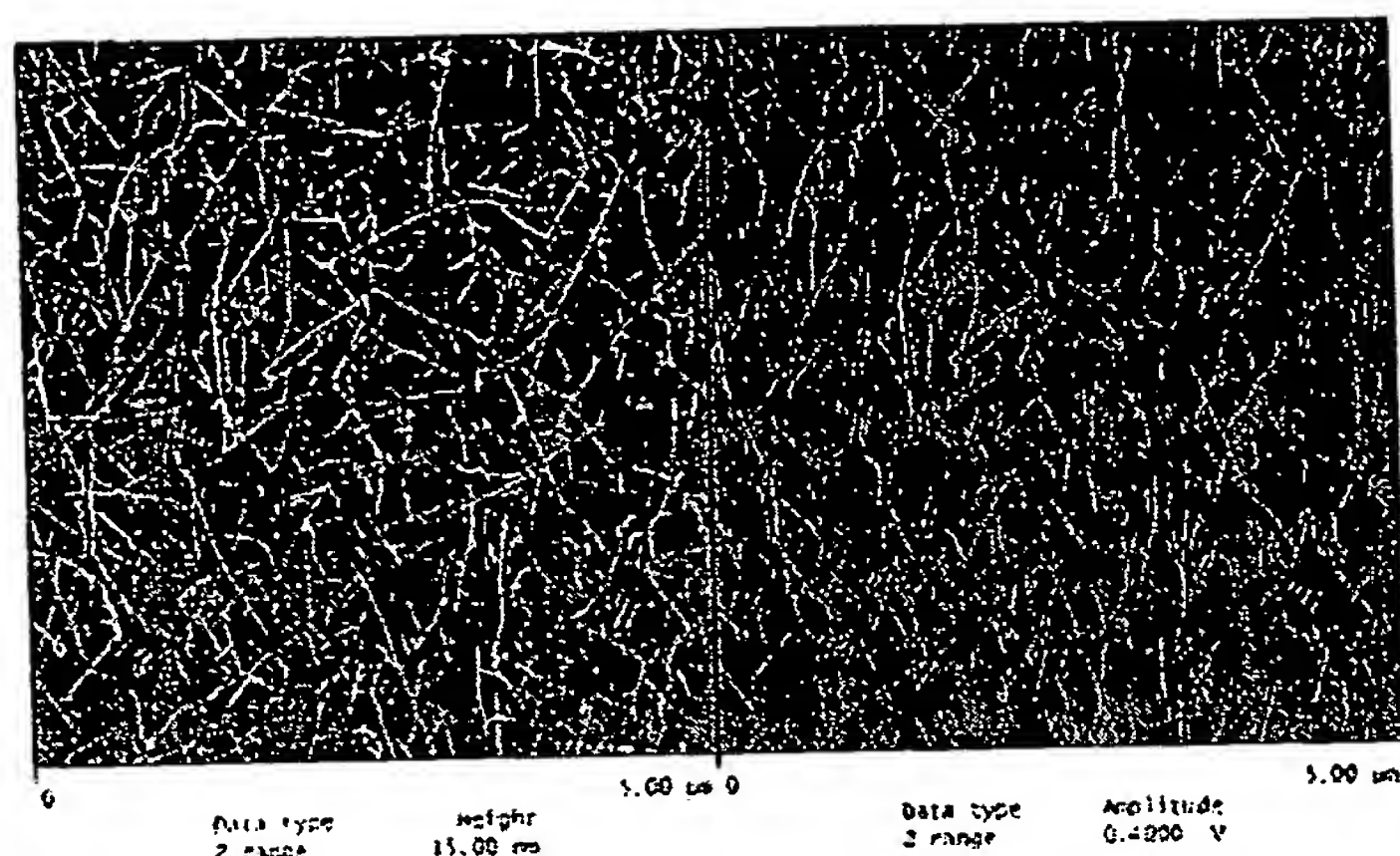


Figure 5. AFM images on mica of the 4-chlorophenyl-substituted nanotubes that were prepared by the SDS/diazonium protocol. Nanotubes were dispersed in DMF, cast and then evaporated to dryness before imaging. (Left) Height and (right) amplitude of functionalized nanotubes (5 μm per box edge).

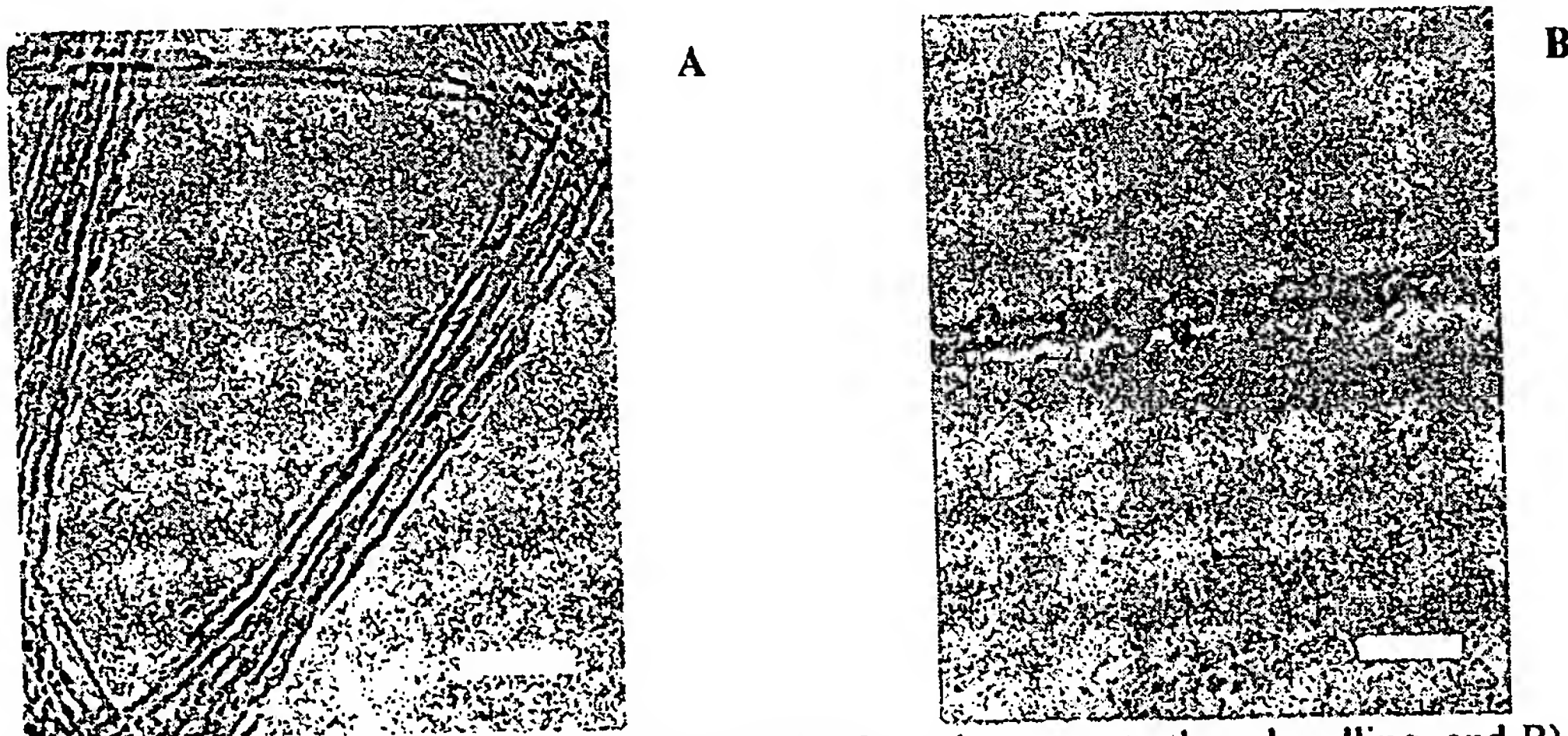


Figure 6. TEM of A) washed, filtered SDS-free SWNT to demonstrate the rebundling, and B) SDS-free 4-*tert*-butylphenyl-substituted SWNT demonstrating their propensity to remain as individualized nanotubes.

5 nm

5 nm

To demonstrate the versatility and functional group compatibility of this protocol, Figure 7 shows just a few of the diazonium salts that have been prepared and added to SWNT sidewalls.

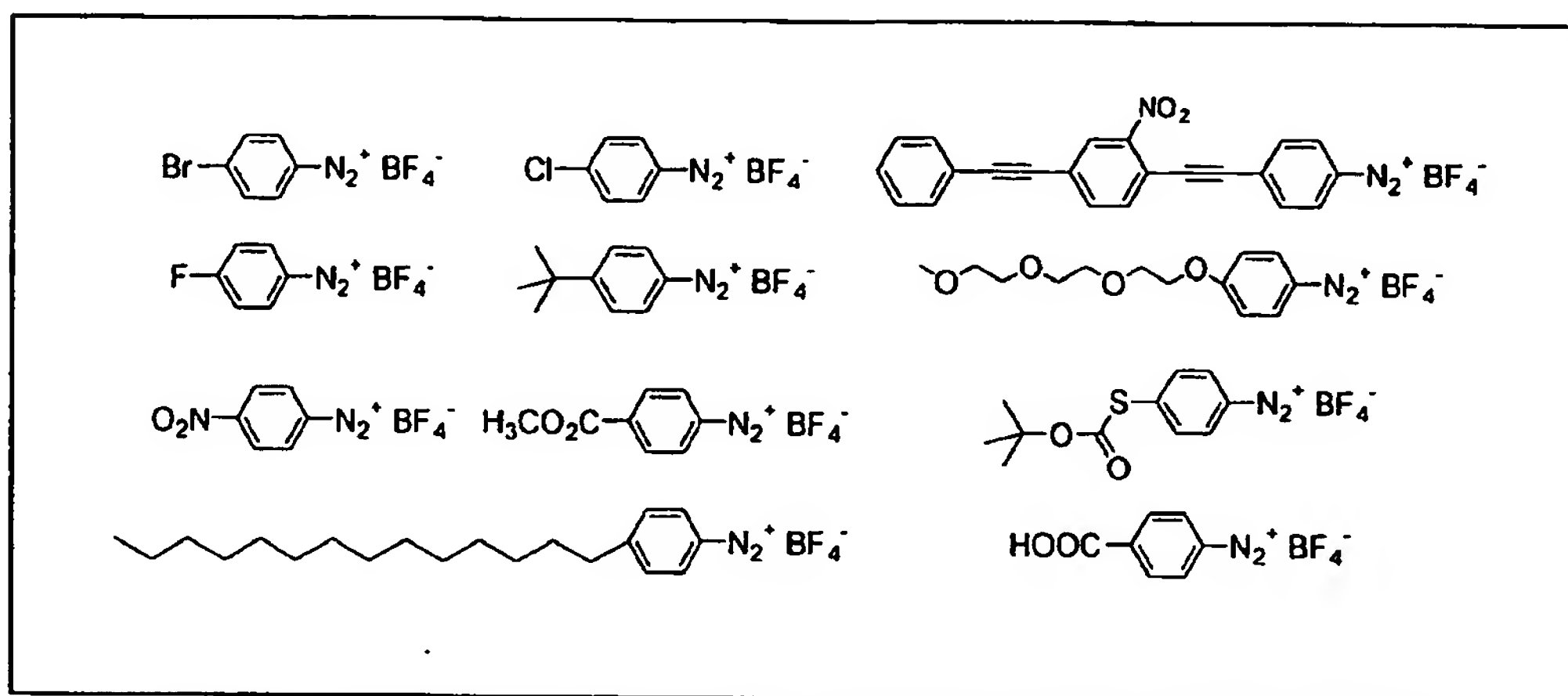


Figure 7. Some diazonium salts that have been added to SWNT sidewalls.

### Vinyl Polymerization From and Alkylation of Functionalized SWNT

We have already demonstrated the ability to form vinyl polymers from the 4-bromophenyl-functionalized SWNT (Figure 8).

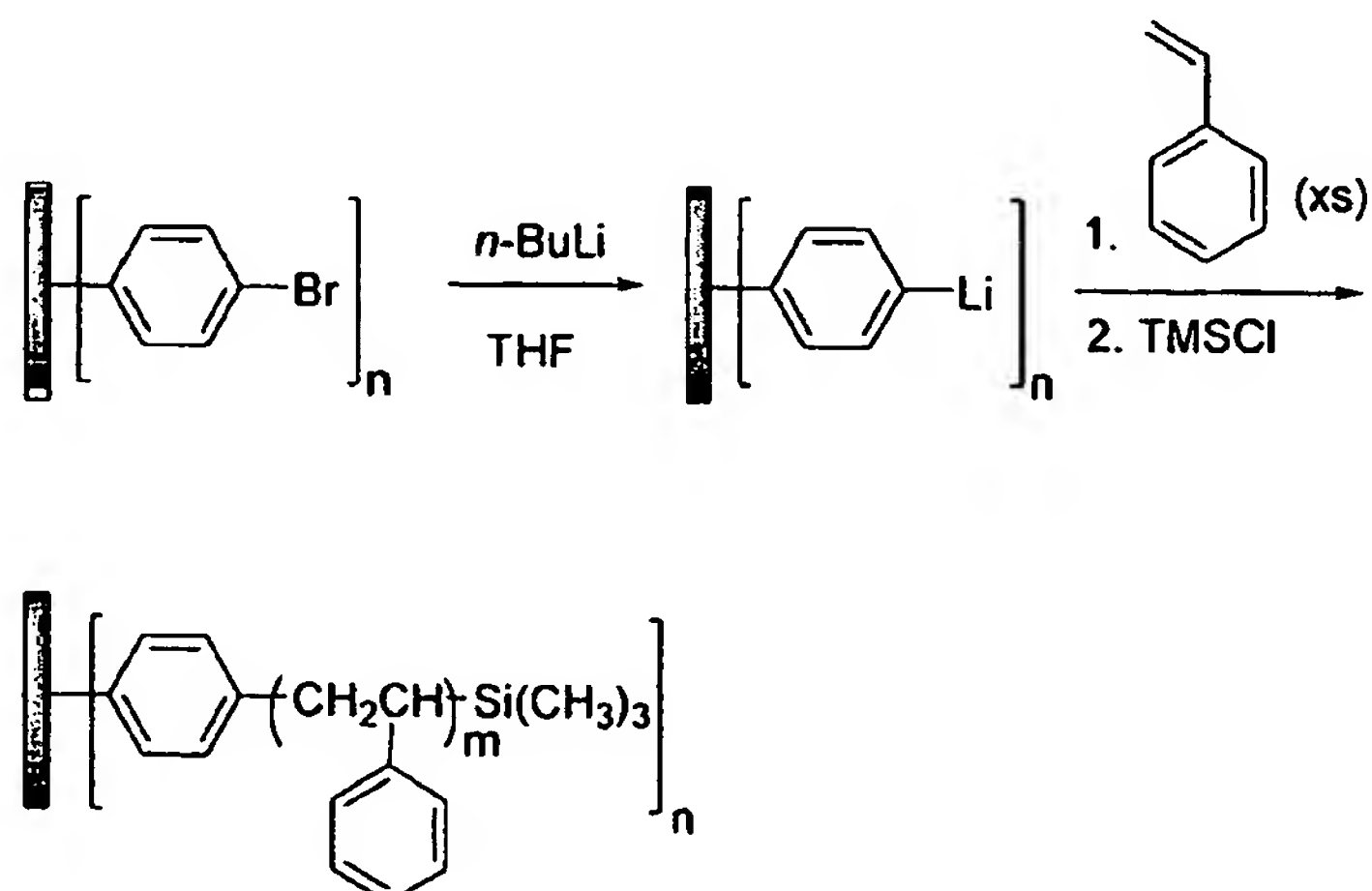
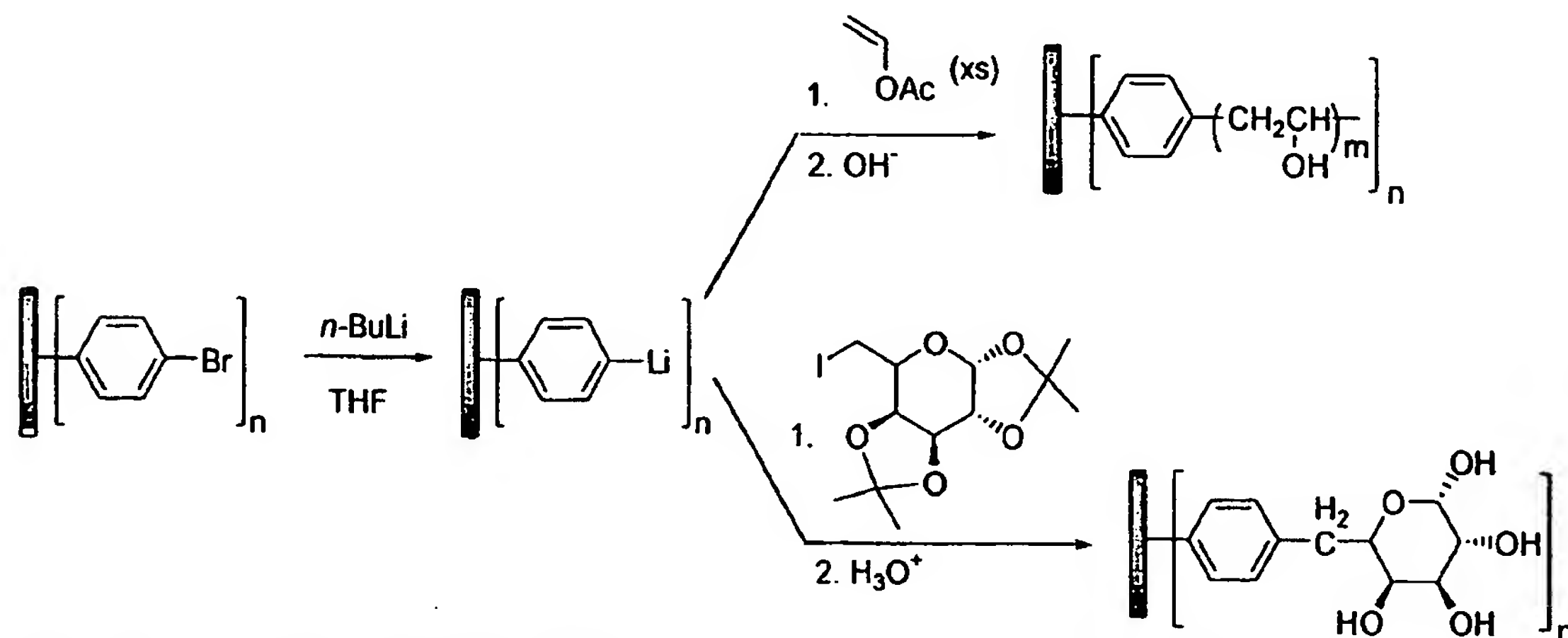


Figure 8. Polymerization of styrene from the sidewalls of SWNT. The molecular weight of the styrene addends is ca. 60,000 as determined by endgroup (trimethylsilyl)  $^1\text{H}$  NMR integration relative to the styrenyl units.

In the same manner, for this project, we plan to react the styrenyl-lithium intermediate with vinyl acetate to generate, after hydrolysis, the poly(vinyl alcohol) (PVA) pendants, as well as quenching with the protected commercially available iodo saccharide to afford, after hydrolysis, the saccharide addends (Figure 9). Both of these systems should be alcohol soluble.



**Figure 9.** Proposed synthesis of PVA and saccharide-functionalized SWNT that are water and alcohol soluble.

In summary, rich and efficient synthetic chemical methods have been devised for the sidewall functionalization of SWNT that afford individualized nanotubes. These pendants can also be made to afford water and alcohol soluble materials, thereby streamlining the SWNT seed-growth effort.

- (1) Saito, R.; Dresselhaus, G.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; Imperial College Press: London, 1998.
- (2) (a) Bahr, J. L.; Tour, J. M. *J. Mater. Chem.* **2002**, *12*, 1952. (b) Banerjee, S.; Kahn, M. G. C.; Wong, S. S. *Chem. Eur. J.* **2003**, *9*, 1898. (c) Liu, T.; Kumar, S. *Nano Lett.* **2003**, *5*, 647.
- (3) (a) Strano M. S.; Dyke C. A.; Usrey M. L.; Barone P. W.; Allen M. J.; Shan H.; Kittrell C.; Hauge R. H.; Tour J. M.; Smalley R. E. *Science* **2003**, *301*, 1519. (b) Dyke, C. A.; Stewart, M. P.; Maya, F.; Tour, J. M. *Synlett* **2004**, *1*, 155. (c) Dyke, C. A.; Tour, J. M. *Nano Lett.* **2003**, *9*, 1215.
- (4) Davis, V. A.; Ericson, L. M.; Parra-Vasquez, A. N.; Fan, H.; Wang, Y.; Prieto, V.; Longoria, J. A.; Ramesh, S.; Saini, R. K.; Kittrell, C.; Billups, W. E.; Adams, W. W.; Hauge, R. H.; Smalley, R. E.; Pasquali, M. *Macromolecules* **2004**, *37*, 154.
- (5) (a) Dyke, C. A.; Tour, J. M. *J. Am. Chem. Soc.* **2003**, *5*, 1156. (b) Bahr, J. L.; Tour, J. M. *Chem. Mater.* **2001**, *11*, 3823. (c) Bahr J. L.; Yang J.; Kosynkin D. V.; Bronikowski M. J.; Smalley R. E.; Tour J. M. *J. Am. Chem. Soc.* **2001**, *27*, 6536. (d) Dyke, C. A.; Tour, J. M. *Chem. Eur. J.* **2004**, *10*, 812.
- (6) Weisman, R.B.; Bachilo, S.M.; Tsyboulski, D. *Appl. Phys. A-Mater.* **2004**, *78*, 1111.
- (7) Dresselhaus, M.S.; Dresselhaus, G.; Eklund, P. *Science of Fullerenes and Carbon Nanotubes*; Academic Press, 1996.



### Task 7: Catalyst Preparation, Attachment & SWNTcat Purification (Barron)

This Task shall prepare and deliver milligram amounts of purified SWNTcat to Tasks 1 and 2 for Amplification. In this phase of our studies we propose to limit the choice of the catalyst component to the iron-molybdenum nanocluster FeMoC  $[\text{H}_x\text{PMo}_{12}\text{O}_{40}\text{C}(\text{H}_4\text{Mo}_{72}\text{Fe}_{30}(\text{O}_2\text{CMe})_{15}\text{O}_{254}(\text{H}_2\text{O})_{98})]$  by Müller and co-workers. (A. Müller, S. K. Das, P. Kögerler, H. Bögge, M. Schmidtman, A. X. Trautwein, V. Schünemann, E. Krickemeyer, and W. Preetz, *Angew. Chem. Int. Ed.*, 2000, 39, 3414.) The structure of FeMoC consists of a tetrahedral reduced Keggin  $[\text{H}_x\text{PMo}_{12}\text{O}_{40}]^{3-}$  ion inside a spherical icosahedral giant cage of the  $\{(\text{Mo}^{\text{VI}})\text{Mo}^{\text{VI}}_5\}_{12}\text{Fe}^{\text{III}}_{30}$  type. In addition to its interesting magnetic properties, Liu and co-workers have shown FeMoC be a suitable catalyst precursor for the growth of SWNT. (L. An, J. M. Owens, L. E. McNeil, and J. Liu, *J. Am. Chem. Soc.*, 2002, 124, 13688.) While desirable as a catalyst, there are several challenges with regard FeMoC synthesis, purification, solubility and reactivity that must be tackled to enable large scale SWNT amplification.

It is important that each catalyst particle that is attached to a SWNT have an identical composition. Significant variation in composition may result in variations in growth rate during the cloning process. In this regard the purification of the FeMoC is important. The as-published synthesis of FeMoC has a low yield ( $< 10\%$ )<sup>1</sup> and there appears uncertainty as to the color (described as either dark blue or greenish) and the solubility and/or stability in various solvents. Such contamination will alter the Fe:Mo ratio, resulting in a potential variation in catalyst activity and growth rate. In addition, the FeMoC is insoluble in most solvents, shows slow reaction with suitable functional groups, and undergoes an undesirable solid state polymerization. These issues are primarily due to the presence of coordinated water on the surface of the FeMoC. In this regard an understanding of suitable ligands for the attachment of FeMoC to a chemically functionalized SWNT is important. We propose to investigate the ligand substitution chemistry of FeMoC.

We note that in addition to cutting the SWNTs, it is equally important to maximize the yield of “active” ends for the SWNTs. By “active” ends we mean those that contain significant numbers of functional groups that will allow for reaction with the FeMoC catalyst. Our initial experiments have shown that using traditional piranha etch results in only 60% of the SWNT forming SWNT-FeMoC conjugates. In order to optimize the formation of SWNT-FeMoC conjugates we propose to investigate alternative end-activation reactions.

Tether FeMoC to open ends of SWNT -to make SWNT-FeMoC conjugate (SWNTcat)

The ability to selectively tether the open end of an activated SWNT to FeMoC is a key step in the specific amplification of SWNT rather than the growth from a catalyst particle. If an individual SWNT is to be cloned then there are several problems that must be overcome. Most importantly, a suitable catalyst must be bound directly to the SWNT in question. Excess catalyst cannot be present since this will allow for growth of new SWNT with no control over diameter/chirality. An additional requirement is that the catalyst be bound on the end of the SWNT rather than attached to the side wall, however, the catalyst may react with the sidewall allowing the formation of two new ends. Additional requirements are that the complex between the transition metal catalyst (FeMoC) and the SWNT must be stable to solvents and handling,

and that the catalyst be of a consistent composition such that growth rates may be controlled for each SWNT.

A key synthetic goal of the proposed research is the creation of suitably functionalized SWNT such that they are soluble and react with FeMoC. However, the groups that solubilize the SWNT cannot preferentially bind FeMoC or multiple FeMoC will bind per SWNT. We propose to investigate several protocols in tandem that will accomplish this goal.

At present a mild piranha etch [a mixture of concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in a volume ratio of 4:1 is used for cutting and activating SWNT. The piranha treatment is thought to give carboxylic acid substituents ( $-\text{CO}_2\text{H}$ ) on the cut ends of the SWNT, although quinone functional groups ( $-\text{C}=\text{O}$ ) have also been proposed. The active component of the piranha etch is peroxysulfuric acid [ $\text{HO}(\text{SO}_2)\text{OOH}$ ], which can be further enhanced by the addition of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (ammonium persulfate) in place of hydrogen peroxide; forming peroxydisulfuric acid [ $\text{HOO}(\text{SO}_2)(\text{SO}_2)\text{OOH}$ ]. (Kern, W., in "Handbook of Semiconductor Wafer Cleaning Technology" (Kern, W. ed.), p. 19. Noyes Publications, New Jersey, 1993.) We propose to investigate the effectiveness of enhanced piranha etch on the yield of SWNT-FeMoC conjugates.

An alternative treatment to piranha is nitric acid and nitric-sulfuric acid etches. We have shown that a mixture of sulfuric and nitric acids rapidly etch (cut) SWNT. Under extended reaction conditions a significant quantity of amorphous carbon is formed, however, we propose that rapid ( $< 1$  min.) reactions should allow for a higher degree of end-activation than observed for the piranha.

Experiments will be carried out using a range of acid etch protocols. The treated SWNT will be sidewall functionalized and exposed to FeMoC solutions under identical conditions. The SWNT-FeMoC conjugate yield will be determined by AFM measurements by counting successful FeMoC-SWNT docking versus free FeMoC and unreacted SWNT.

#### FeMoC synthesis

The synthesis of FeMoC is a one-pot process involving the reaction of  $\text{FeCl}_2$ ,  $\text{Na}_2\text{MoO}_4$ ,  $\text{HPMo}_{12}\text{O}_{40}$ , and glacial acetic. After adjusting pH the FeMoC slowly precipitates (2-4 days) from solution. As prepared FeMoC is contaminated with significant impurities, however, we have shown that Soxhlet extraction of the reaction mixture with EtOH yields highly pure FeMoC with EtOH ligands (FeMoC-EtOH). (R. E. Anderson, D. Ogrin, E. Whitsitt, M. Stewart, C. L. Edwards, V. C. Moore, R. E. Smalley, J. M. Tour, and A. R. Barron, in preparation.) An advantage of our method of purification is that EtOH ligands are much easier to remove from the coordination sphere of FeMoC than coordinated water ligands. Thus subsequent reactions with the activated SWNT are possible and enabled. The EtOH ligands are readily displaced by ligands containing suitable substituents such as carboxylate groups, thiols, and pyridines. The extent of the substitution is dependent on the relative strength and binding constant of the ligand.

Problems with the synthesis include: optimization of the yield (minimization of side products), scale-up, decrease in reaction time, and the activation towards reaction with SWNT. We have shown that FeMoC has a distinctive  $^{31}\text{P}$  NMR. We propose to use  $^{31}\text{P}$  NMR to follow the synthesis of FeMoC using a matrix approach (due to the number of potential variables including: ratio of reagents, concentration, pH, temperature, and reaction time). Although FeMoC-EtOH shows a solubility of 17.8 mg/mL in EtOH we propose to study the effects of alternative weakly coordinating ligands on the solubility in EtOH. The choice of a suitable leaving group should also enhance the yield of the SWNT-FeMoC conjugate. Thus, once the optimum conditions have been determined we will exchange the EtOH ligands with alternative leaving groups (initial studies will be aimed at other alcohols and glycols) and the solubility and reactivity of these substituted FeMoC derivatives will be studied. We have shown that characterization of substituted FeMoC is readily accomplished using a combination of AFM (particle size), TGA (FeMoC:L ratio) and IR/Raman spectroscopy.

#### FeMoC attachment to open end of SWNT seed

As a general protocol the attachment of FeMoC to the ends of the activated SWNT will be via a suitable functional group that will bind with a sufficiently high  $K_{\text{eq}}$  to the FeMoC. Based upon our initial studies the most likely point of attachment will be the 30  $\text{Fe}^{\text{III}}$  centers on the surface of the FeMoC. It is these centers to which the EtOH substitution of water occurs. In order to promote attachment of the SWNT to FeMoC we propose to chemically functionalize the SWNT with suitable ligands. In addition, while the ends of a SWNT may be considered to be a multi-dentate ligand (and hence enhance binding through the chelate effect), the position of the reactive groups is also important to optimize the number of potential binding sites. Molecular modeling indicates that short linkage units (the moieties between the SWNT and the functional group that binds to the FeMoC) will limit the potential binding sites. In contrast, increasing the linkage by a  $\text{C}_2\text{H}_4$  unit will allow for coordination to more  $\text{Fe}^{\text{III}}$  centers on the FeMoC (enhancing the binding), see Fig. A. We propose to investigate a number of alternative functional groups and optimize the selectivity of binding.

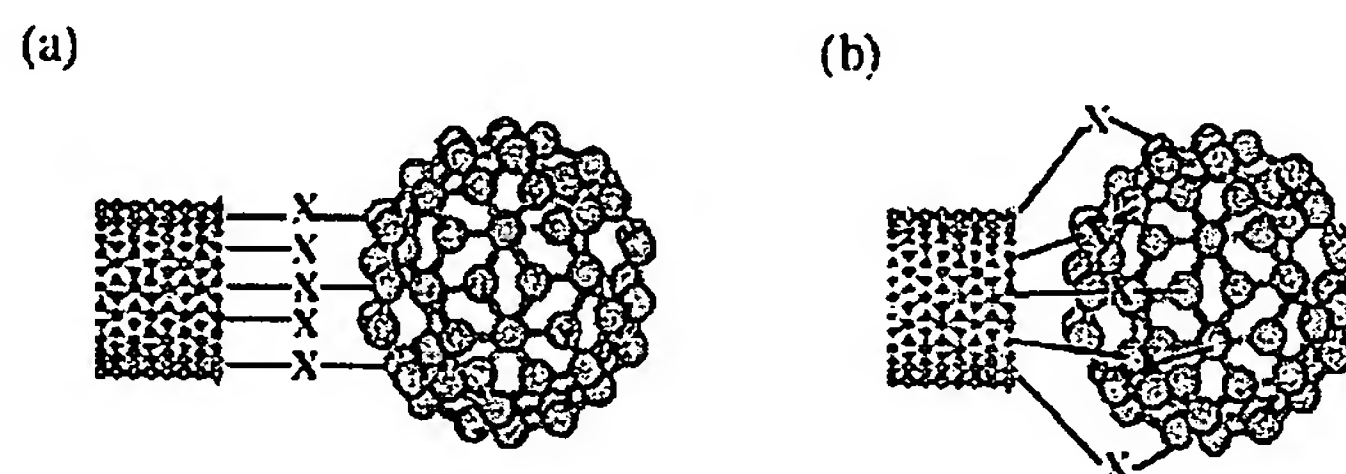


Fig. A. Schematic representation of the availability of ligands to FeMoC as a function of linkage length.

One of the most important issues with regard linkage groups is any competition between binding to the end groups (desirable) versus the stabilizing/solubilizing groups on the sidewall (undesirable). Our present protocol uses sulphonate groups to allow the SWNT to be soluble. We have shown that these bind weakly to FeMoC, however, the binding to carboxylic acid groups appears to be preferential to that of the sulphonate. We propose to undertake competition



experiments with any functional group that provides the desired solubility to the SWNT (e.g., sugar, glycol, hydroxide) with regard the terminal binding groups.

#### Carboxylic acid linkage group

The easiest linkage group to FeMoC is the carboxylic groups that are formed during acid and oxidative treatment. We have demonstrated that carboxylic functionalized SWNT react with FeMoC to form a SWNT-FeMoC conjugate complex. Based upon separate studies we have shown that carboxylic acids, such as octanoic acid, readily substitute the EtOH ligands and bind to FeMoC. Thus, the carboxylic acid linkage unit is the base line to which others will be compared.

We propose to use Mössbauer spectroscopy to characterize the interaction with the FeMoC as well as study the effects of various acid treatments to maximize the efficiency of binding.

#### Alternative substituents thiols and pyridines

Our studies of ligand substitution on the surface of FeMoC suggest that the most suitable ligands (besides carboxylic acids) are thiols and pyridine derivatives. In this regard we propose to study the synthesis of functionalized SWNT and their binding to FeMoC. For simplicity the functionalization protocols will be based on the reaction of the carboxylic acid groups on the cut SWNT. In this regard the type and length of linkage group will be changed but not the number or extent of functionalization.

We have made an initial investigation of this approach. The reaction of carboxylic acid functionalized SWNT with 2-aminoethanethiol hydrochloride (2-AET·HCl) results in the formation of an amide linkage and a terminal thiol available for coordination to FeMoC (Fig. B). We propose to extend this study to vary the length of the organic linkage to allow for optimal binding of the FeMoC (see Fig. A) and the use of pyridine based ligands (Fig. B).

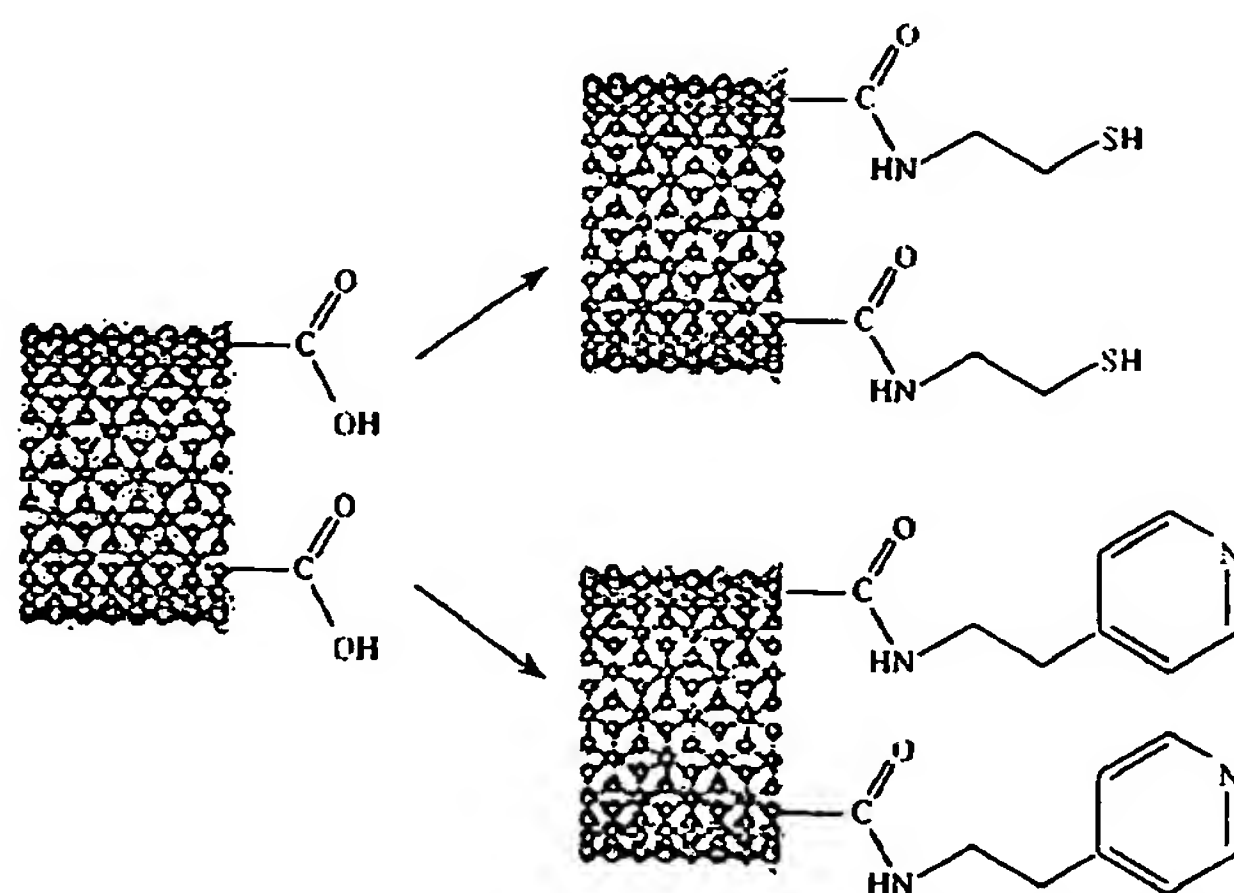


Fig. B. Reactions of carboxylic acid derived SWNT to provide thiol and pyridine functionalization to SWNT.

Characterization will be by AFM, XPS and Mössbauer (which may allow for the differentiation of Fe-O versus Fe-N and Fe-S complexation). In order to demonstrate the irreversibility of the binding we will “wash” the SWNT-FeMoC conjugate with a suitable mono-dentate ligand. The length of the linkage group will be varied through normal synthetic means and the efficacy of complexation studied.

The reaction conditions will be varied to allow for optimization of SWNT-FeMoC conjugate formation. We have previously shown that an increase in reaction temperature significantly increases the extent of conjugate formation. This would suggest that the reaction is essentially a dissociative process, i.e., dissociation of EtOH from the FeMoC and subsequent association of the functionalized SWNT. Other factors to be investigated include: concentration effects, reaction time, solvent, and the ligand present on the FeMoC.

#### Quinoid carbonyl SWNT termination

It has been reported quinone functional groups are formed on the ends of SWNT during cutting. These will offer an alternative synthetic methodology to the addition of linkage groups (in particular condensation reactions). We propose to investigate the functionalization of SWNT by reactions that are specific to quinones (ketones). The goal here is to optimize the linkage to the SWNT rather than the actual complexation agent (i.e., thiol versus pyridine etc.).

#### Purification of SWNTcat solutions

We have demonstrated that FeMoC and ligand substituted FeMoC (i.e., FeMoC-L where L = octanoic acid, hexanethiol, and 3-butylpyridine) may be separated from solution using room temperature centrifugation at 4400 rpm for 5 min. Given that the density of the SWNT-FeMoC should be significantly different than the FeMoC, we propose that differential centrifugation offers potential for separation of SWNT-FeMoC from unreacted FeMoC.

We have shown that FeMoC binds strongly to gold surfaces and is not removed by the addition of typical SAM ligands such as thiol. In contrast substituted FeMoC appears to show far less absorption to gold. We propose that the removal of unreacted FeMoC may be possible through precipitation on gold. We propose to study the separation of FeMoC/SWNT-FeMoC solutions by adsorption.

The solubility of FeMoC and its ligand-substituted complexes (FeMoC-L) appear to be quite different. If the solubility of SWNT-FeMoC conjugate is largely unaffected by the presence of additional ligands on the FeMoC, then the reaction with a suitable ligand may promote the precipitation of FeMoC not complexed to SWNT, without the conjugate disruption (Fig. C). The key issues to be resolved will be the retained solubility of SWNT-FeMoC-L and the stability of the SWNT-FeMoC interaction in the presence of L. The latter should not be an issue given the stability of the multi-dentate ligand over mono-dentate ones (chelate effect).

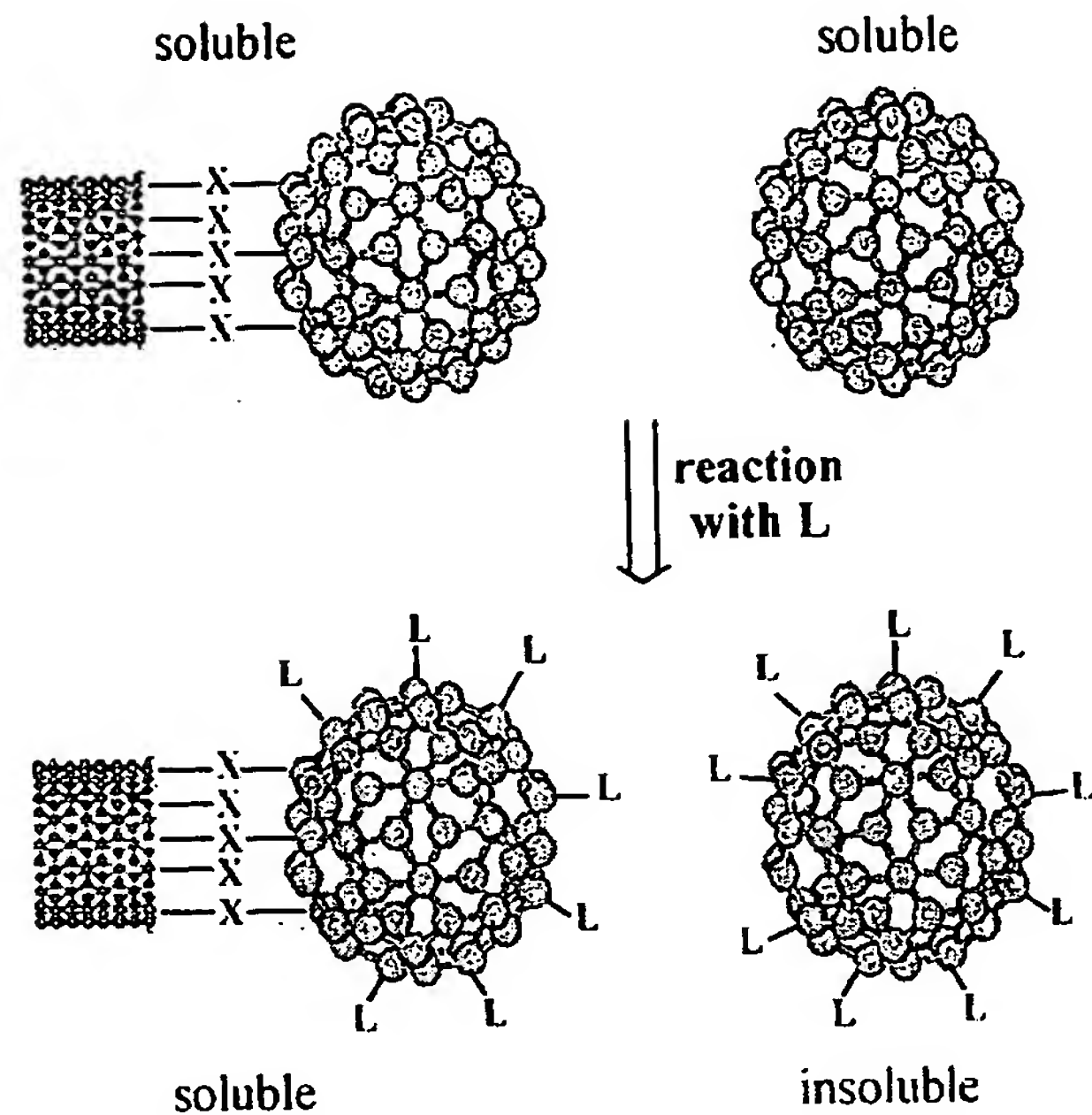


Fig. C. Selective precipitation of FeMoC from SWNT-FeMoC.

Task 8: Project Management & Reporting (Smalley, Schmidt)

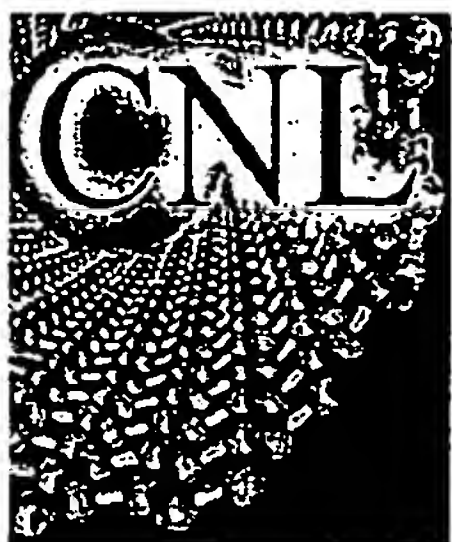
R. E. Smalley, Principal Investigator and Technical Contact will perform technical project management. H. K. Schmidt, Administrative Contact, will perform financial management and project reporting. We plan to monitor and guide progress through a combination of bi-weekly meetings of the whole Project Team, weekly meetings of each Task Team and written monthly progress reports from each Task Team. These monthly Task reports will be combined with an overall summary to generate informal monthly progress reports to the Program Manager at DARPA. A formal written Final Report will be delivered to DARPA upon completion of the six-month project, along with a personal presentation at DARPA headquarters.



## **Statement of Work**

The project team shall perform research on demonstrating SWNT Amplification by growing nanotube material from short SWNT seeds and chemically specific catalysts. The investigators shall prepare and deliver monthly and final technical reports of progress and results. The Principal Investigator shall prepare and deliver a personal presentation to the DARPA Program Manager. The work will be organized according to the Technical Tasks:

1. Construct and operate apparatus for SWNTcat growth on supports; characterize product materials.
2. Construct and operate apparatus for SWNTcat growth in gas phase; characterize product materials.
3. Produce, purify, type-tune and characterize SWNT starting material
4. Produce and characterize short SWNT
5. Develop SWNT functionalization chemistries for ethanol solubility via Birch alkylation
6. Develop SWNT functionalization chemistries for ethanol solubility via diazo arylation
7. Produce FeMoC; develop tether chemistries; produce and purify SWNTcat.
8. Project management and report generation.



## ARMCHAIR QUANTUM WIRE: DIRECTED RESEARCH & DEVELOPMENT

CARBON NANOTECHNOLOGY LABORATORY  
Rice University – Houston, Texas, USA

### Introduction

We propose a highly directed five-year program to develop scaleable production, processing and manufacturing technologies for Armchair Quantum Wire (AQW). We envision AQW as a large quasi-crystalline assembly of specific Single Wall Carbon NanoTubes (SWNT) optimized for maximum electrical current carrying capacity. We fully expect that AQW will have at least the conductivity of copper at one-sixth its weight. Recent research results indicate that further order-of-magnitude improvements may be possible as well. The program has a firm foundation in the pioneering SWNT production, characterization and processing technology- and experience-base in Prof. Smalley's Group, the Carbon Nanotechnology Laboratory (CNL) team and collaborating institutions. Armchair Quantum Wire represents an important opportunity with potentially transformative impact across both Federal and Private sectors; a few are listed here:

Aerospace  
Electric Propulsion  
Power Distribution

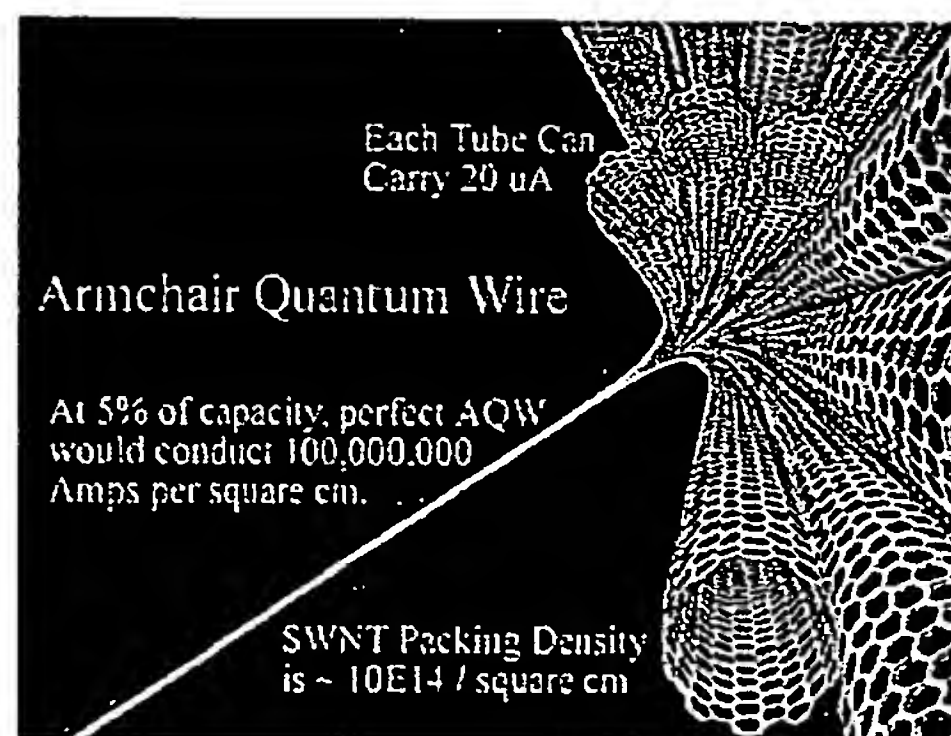
signal wiring, power harnesses and actuators  
primary drive motors, regenerative braking, servo systems  
high-power, long-distance power grids

Air Force, NASA, MDA  
Army, Navy, DOE/DOT  
DOE, FERC

Since SWNT are a pure carbon polymer with extremely attractive chemo-mechanical properties, AQW will enjoy a number of primary and multi-functional advantages compared to industrial alternatives, primarily copper and aluminum and their alloys. A representative list of material properties and potential impact follows:

Property	AQW / SWNT	Copper	Aluminum	Potential Impact
Electrical Conductivity	$10^4$ - $10^7$ mho	$5.3 \times 10^5$ mho	$3.8 \times 10^5$ mho	20-50% smaller, lighter motor/generators
Mass Density	1.4 g/cc	8.9 g/cc	2.7 g/cc	10-100 x lighter signal/power harnesses
Environmental	inert to 500C	corrodes	surface oxides	reduced maintenance, especially at sea
Thermal Expansion	-2 ppm $^{\circ}\text{C}^{-1}$	16 ppm $^{\circ}\text{C}^{-1}$	23 ppm $^{\circ}\text{C}^{-1}$	eliminate sagging cables in power grids
Thermal Conductivity	20-2000 $\text{Wm}^{-1}\text{K}^{-1}$	$< 400 \text{ Wm}^{-1}\text{K}^{-1}$	116-235 $\text{Wm}^{-1}\text{K}^{-1}$	thermal mgmt. multi-functional potential
Tensile Strength	5-20 GPa	0.4-1.5 GPa	0.1- 0.6 GPa	laminate multi-functional potential
Bulk Modulus	300-600 GPa	$\sim 30$ GPa	$\sim 80$ GPa	structural multi-functional potential

While our key objective, Armchair Quantum Wire, is both well-defined and clearly practical, we expect that the program will have positive, or even enabling, impact on many other SWNT application areas. These indirect benefits will arise from advances in key unit-processes, e.g. SWNT selection, cutting, cloning, production scaling, cleaning, processing and fabrication. Known SWNT application areas synergistically impacted will include fuel cells, ultra-capacitors, nano-electronics, structural composites, photovoltaics, sensors and bio/medical applications. Indeed, this effort will generate a transformative technology platform supporting many applications of this hyper-versatile engineering material, Single Wall Carbon NanoTubes.



The Armchair Quantum Wire concept is well grounded in oft-repeated observations of quantum, ballistic electron transport in individual metallic nanotubes at current densities above  $10^9$  amps per square centimeter – several orders of magnitude better than copper. This behavior is a direct and unique consequence of the nanometer-diameter, cylindrical structure and molecular perfection of the basic SWNT molecule. In essence, electrons can

only travel along the axis of the nanotube. For symmetry reasons, the typical electron scattering and energy loss mechanisms found in common metals simply do not exist in this material. Thus, properly selected SWNT can act like 'optical fibers for electrons', guiding high currents efficiently.

Practical AQW will consist of quasi-crystalline bundles of nanotubes of finite length. Calculations have shown that neighboring, aligned nanotubes will enjoy efficient tube-tube conduction through resonant quantum tunneling, as long as the tubes are of identical structure. This will largely bypass reflection effects at the ends of individual nanotubes – and provide a mechanism to preserve the quantum wires' microscopically outstanding conduction throughout the bulk of a macroscopic array of nanotubes. This does imply however, that we will have to fabricate AQW out of only one of the many types of available nanotubes.

Success in this venture will therefore also depend on developing a SWNT production process that delivers specifically structured SWNT. About one third of the possible SWNT structures exhibit metallic conduction. Of these we will focus on the "Armchair" family, depicted in the concept sketch above. Among SWNT, Armchair tubes have the highest density of allowed electron energy states, and have been predicted to be essentially impervious to defects, bends and similar imperfections that will inevitably occur in real-world macroscopic objects. Armchair tubes are also achiral and completely axially symmetric, ensuring that the conditions for resonant quantum tunneling are preserved in bulk articles.

Our approach for producing exclusively Armchair tubes efficiently and at low cost is called 'cloning'. In SWNT cloning, desired type(s) are selected from a now-typical SWNT mixture and propagated. Tubes are chemically cut into very small segments (20 nm) and "amplified" back to full production length (microns to tens of microns). We expect single-cycle gains on the order of one thousand or more in this system, as explained in detail below. This will enable bulk production of selected SWNT (Armchair tubes) starting from a very small quantity of material selected by chromatographic or similar means.

SWNT production processes to be perfected in this work will employ extremely low-cost feedstocks (e.g. CO/H<sub>2</sub> or methane) and moderate conditions (e.g. 600 °C at 500 psi). SWNT synthesis is catalyzed by inexpensive transition metals (e.g. iron, cobalt or molybdenum). Thus, the full-scale process and plant should be similar to those used for producing high molecular weight polyethylene, one of the cheapest industrial polymers. SWNT processing technology for making the final wire and cable products will most likely be based on fibers spun from concentrated sulfuric acid (oleum), another very inexpensive industrial chemical. This is the essentially the same technology used for spinning Kevlar and Zylon fibers affordably at the ton-scale.

At CNL, we think of Buckytubes as a new polymer of pure carbon, in the tradition of the great "miracle polymers" of the last century like Nylon, polypropylene and Kevlar. We expect that Buckytube production technology will follow a path similar to theirs. Initially, each of these polymers was produced in small amounts at low yield with many impurities. Today, these materials are produced in vast quantities around the world quite cheaply with extraordinarily efficient and elegantly specific catalysts. We believe that the new miracle polymer, Buckytubes, has a similar destiny. A key goal at CNL is to develop the processes that permit such rapid Buckytube development, and we believe the key break-through will come from prepared catalysts and growth from seeds. This approach will enable low-cost production of SWNT with total control over type, diameter and length under moderate conditions using cheap feedstocks like Syngas derived from coal.

The CNL Team at Rice is extremely well qualified and positioned to successfully execute this program. The Laboratory focuses the efforts of ten senior Rice faculty and their groups related to SWNT research and development. CNL was organized in 2003 as a unit of Rice's Center for Nanoscale Science and Technology (CNST). CNL team members are clearly leaders in carbon nanotube R&D, having developed three of the four known SWNT production methods, commercialized HiPco to the pound level, developed several robust SWNT functionalization chemistries, elucidated the basic signatures and spectroscopy of individual SWNT types, and developed superacid-based methodologies for spinning neat and composite SWNT fibers, among many other ground-breaking accomplishments. The program will be led by Professor Richard Smalley, Nobel Laureate and Director of the CNL. Co-Investigators will include additional CNL faculty from Rice University, faculty from collaborating universities, and researchers at Federal laboratories. We estimate financial support for the five-year program at \$25 million.



## Enabling Synergies

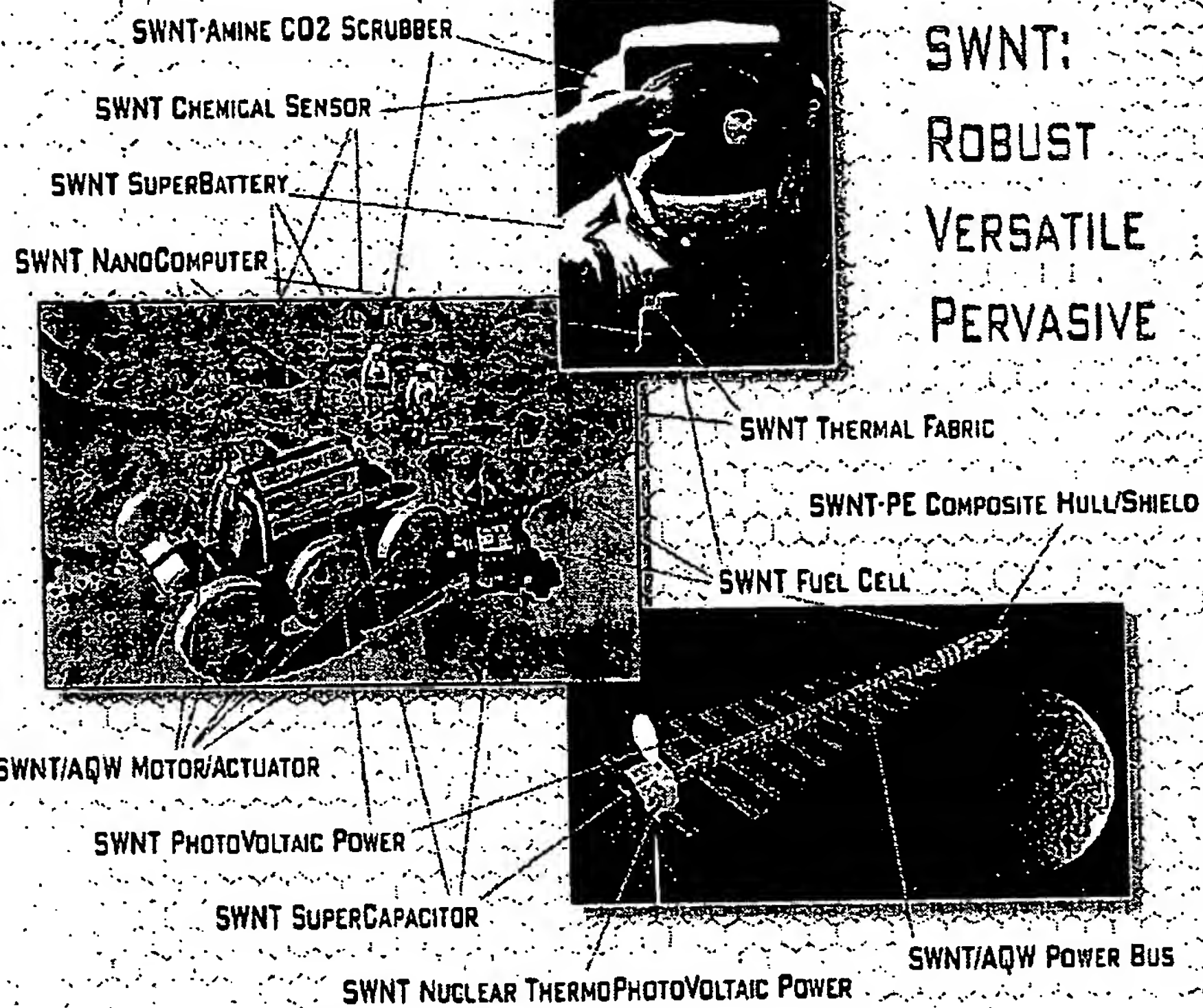
Success in the Quantum Wire program will have wide ranging benefits for Buckytube science, technology and applications well beyond the wire itself. The two broad enabling results of the program will be (n,m) control and substantial production cost reductions due to Cloning. We estimate that the cost target for type-selected SWNT for Quantum Wire should be about \$30 per kilogram – the cheapest application class in the table below. Most SWNT applications can be optimized by using a specific type or class of SWNT, like ESD composites and super-capacitors.

Indeed, some SWNT applications are simply impossible without exact (n,m) control and other technical capabilities to result from this program. For example, consider SWNT transistor arrays. This application requires supply of extremely pure SWNT of exclusively one (n,m) semiconducting tube – and these should be of a very well defined length. For processing, these will have to be solubilized through sidewall functionalization chemistries. For arrays assembly, these will also need different and specific chemical functionalizations on each end. All such functionalizations will also have to be very cleanly removable to yield pristine buckytubes with well defined electronic and optical properties. Finally, low resistance contacts, as needed for AQW will be needed to connect these nanotube elements into circuits.

We have a high degree of confidence that SWNT Armchair Quantum Wire could revolutionize the world of electrical power and signal transport. Even if it does not meet our full expectations, however, the technology developed during this program will enable many other valuable applications and capabilities, and firmly establish Buckytubes as routine engineering materials. The following table shows a non-exhaustive list of potential SWNT applications and estimated cost, type, functionalization requirements.

SWNT Requirements	SWNT cost \$/ kilo	(n,m) control	(I) control	purity # nines	Additional requirements
<b>SWNT Applications</b>					
Bio-Probes/Therapies	30,000	yes	precise	6	extreme purity, end func.
Chemical Sensors	10,000	yes	some	6	mult. types, full func., directed assy.
Molecular Electronics	3,000	yes	precise	6	semis, full func, directed assy.
Photovoltaics	3,000	yes	some	6	semis, end func.
Electronic Interconnect	1,000	yes	some	5	metals
Photocatalysts	1,000	yes	some	4	
Heat Pipes	1,000	yes	no	2	long SWNT, cont. growth, non-metals
Aero signal/power buss	100	yes	no	3	
Heat Sinks/Spreaders	100	no	no	3	long SWNT, membranes, non-metals
Advanced Batteries	30	yes	no	2	metals, controlled dia./spacing
Supercapacitors	30	yes	no	3	metals, controlled dia./spacing
Hydrogen Storage	30	yes	no	3	controlled dia./spacing
High Performance Fibers	30	no	yes	3	
Power Grid Cable	30	yes	no	3	
3D Structural Composites	30	no	no	3	
ESD Composites	30	no	no	2	

## BUCKYTUBES IN HUMAN AND ROBOTIC EXPLORATION

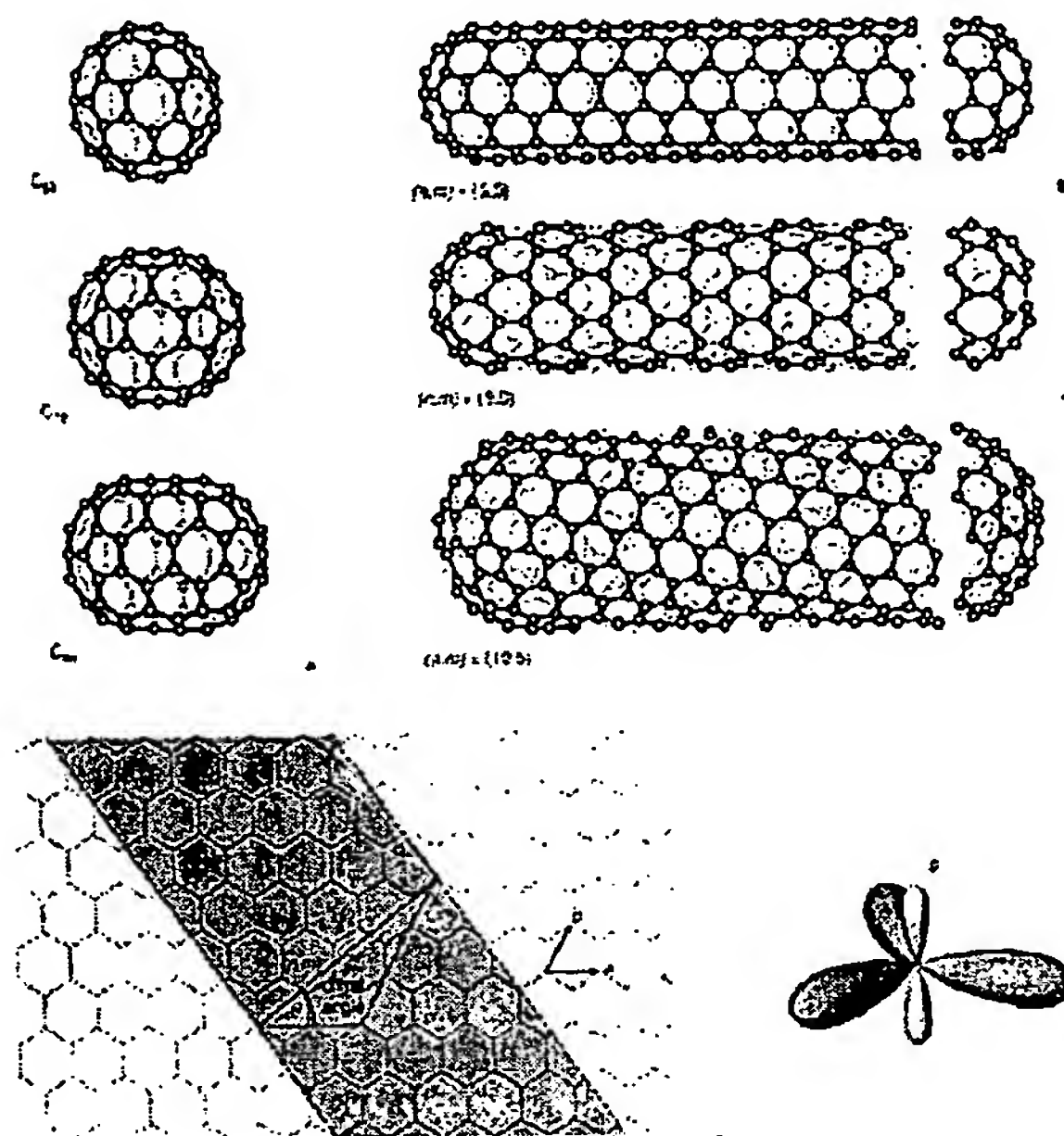


Potential SWNT Applications Span Many Human and Robotic Exploration Capabilities.

## Technical Background & Approach

**Single Wall Carbon Nanotubes (SWNT).** SWNT comprise a class of potentially ideal nano-engineering materials for a wide range of disciplines. While SWNT research and development is aggressive world-wide, and accelerating rapidly, key barriers to full-scale exploitation remain - primarily cost, purity and processing. The economic impact and defense capabilities enabled by resolving these issues successfully are significant. These factors combine to make a compelling case for establishing an intense research and development program encompassing production, processing and manipulation of selected SWNT types, the subject of this proposal.

SWNT [1] are family of cylindrical pure-carbon polymers roughly one nanometer in diameter; individual molecules can range in length from a few nanometers to over one centimeter. One can envision these 'Buckytubes' as being rolled-up from a slice of 'graphene' sheet, with Buckyball halves at the ends. The basic graphene strip can be 'cut' at various angles and of various sizes - resulting in designs for the roughly 100 observed types of Single Wall Carbon Nanotubes. SWNT in general are the strongest and toughest material possible; SWNT also display extremely high thermal conductivity along their axis. Depending on their exact bonding pattern, individual SWNT molecules display a variety of electronic configurations: metallic, semiconductor, or semi-metal. Metallic tubes are among the best conductors known; the semi-conductors have direct band-gaps and extremely high carrier mobility [10]. Insulating tubes can also be produced by organic chemical modifications. SWNT also have the highest possible surface area of any material, since every atom is accessible on the outer tube surface as well as the interior pore.



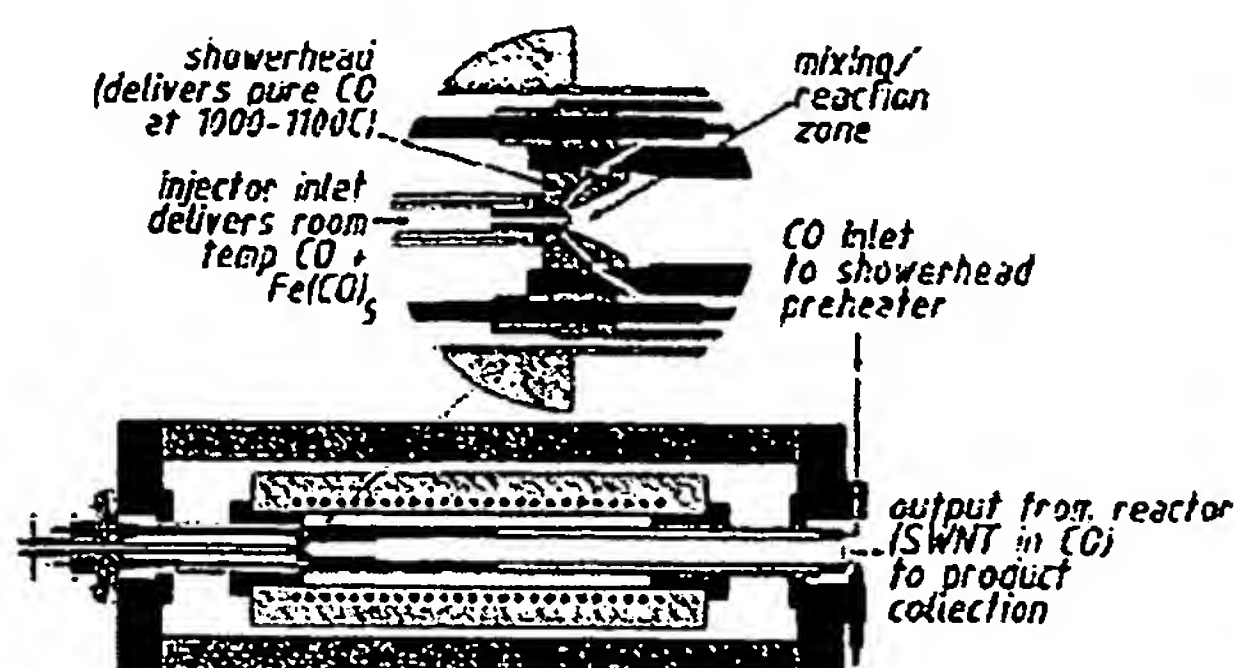
Many applications exploiting their extreme physical properties [2,5,6,7] (strength, toughness, conductivity, carrier mobility, surface area, etc.) have been demonstrated or are under development. Macro-scale applications include high performance composites, conductive polymers, morphing structures and electrodes for fuel cells and supercapacitors; nano-scale applications include sensors, emitters, interconnect and transistors. SNWT surely represent the ultimate in multi-functional materials: one basic material system provides metals, insulators and semiconductors as well as elements bridging nanometer to macro-scale systems.

SWNT production has progressed a long way since their fortuitous discovery in arc soot in 1991 [3,4]. The leading process for making SWNT, called HiPco (High Pressure CO), was developed at Rice in Prof. Smalley's laboratory. The process has been transitioned to commercial operation, with production rates between and 20 and 50 pounds a day expected in mid-2004. Nanotubes grow from nanometer-diameter transition metal catalyst particles (typically Iron), which are generated *in-situ*, e.g. by pyrolysis of iron pentacarbonyl. Carbon is continuously supplied in the form of CO at high pressure; at reaction temperatures (about 950 C), CO dissociates on the catalyst surface to C and CO<sub>2</sub>. As carbon accumulates on the catalyst particles, it forms partial fullerene shells; some of these detach from the metal and serve as the nucleation site for Buckytube growth. Under the influence of the catalyst particle, the free carbon is essentially polymerized onto the growing nanotube, which grows at locally phenomenal rates: around 1 mm per second. Nucleation is rather inefficient and certainly inexact, but the fast growth rate ensures that the bulk of the product is indeed Single-Wall Carbon Nanotubes of high molecular perfection.

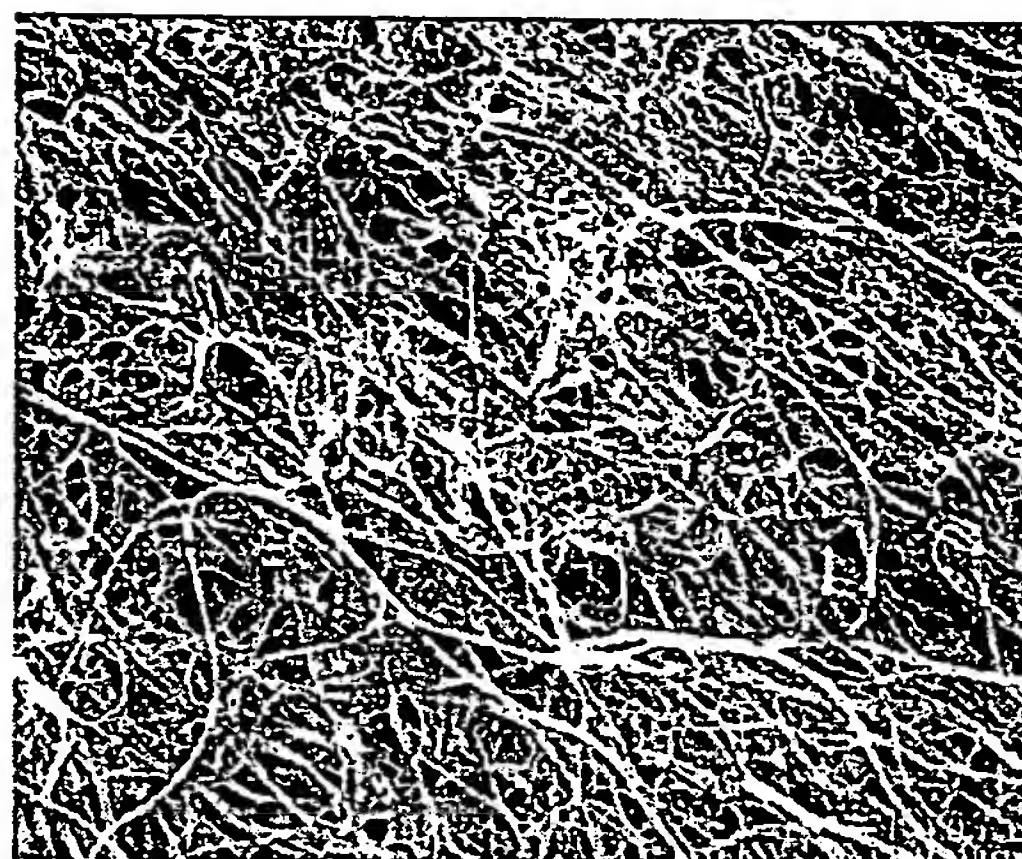
Raw SWNT material (from all sources) therefore contains not only a mixture of SWNT types (n,m) bundled into primordial 'ropes', but also left-over metal catalyst, fullerene shells of many sizes, and metal particles over-coated with relatively thick layers of graphite. These by-products have to be removed by laborious purification steps



before the SWNT material can be used for most applications. The process and its nominal product are shown in the following figure.

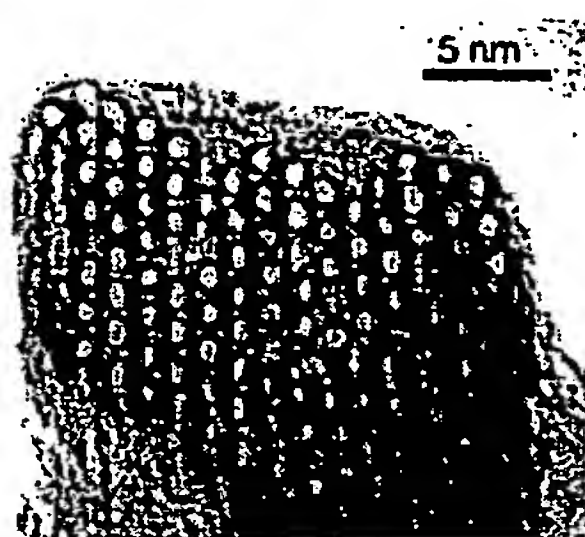


HiPco Is The Standard SWNT Production Technology Today

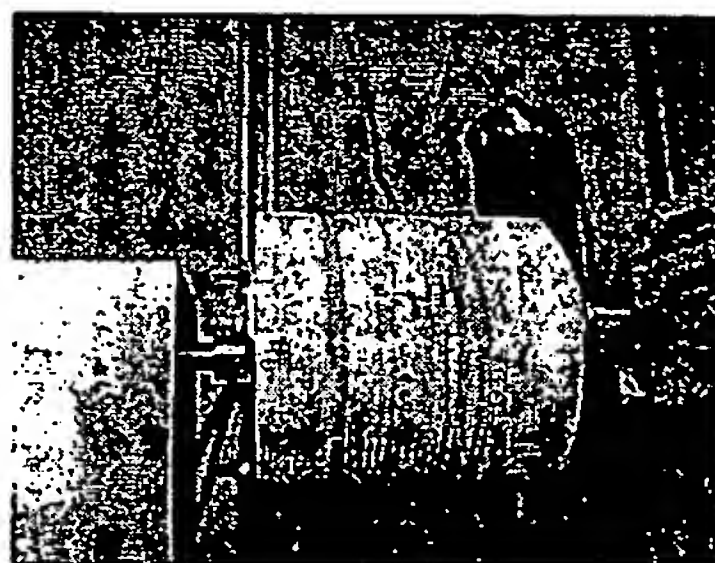


Raw HiPco Product Is A Mat Of SWNT Ropes

**Processing & Spinning.** CNL has pioneered cleaning and post-processing technologies for fabricating both nano-derivatives and macro-scale articles out of SWNT building blocks. This is not without its challenges. SWNT are extremely polarizable and display very strong Van der Waals attraction for one another – hence their famous tendency to aggregate into quasi-crystalline ‘ropes’. The VDW energy is roughly 0.5 eV per nanometer of a pair of tubes in contact. Under cavitation conditions SWNT can be completely separated by surfactants at low yield [8]. We have demonstrated that super-acids, e.g. oleum, can effectively intercalate and ‘lubricate’ ropes, allowing for processing into films and fibers [9]. This provides a key starting point for forming wires and cables from future, optimized SWNT materials. Figures illustrating ropes and oleum-spun neat SWNT fibers follow:



Hexagonal SWNT Self-Assembly



SWNT Fibers Spun From Oleum



SWNT Fiber & “Super-Rope” Detail

**SWNT Type (n,m) Complexity.** We stated above without detail that SWNT come in many different ‘roll-up’ configurations – in fact, there are some 58 observed types to date. Each (n,m) configuration has a very specific spectroscopic signature, and demonstrates the number of electronically distinct SWNT types [18]. The following Figures show a ‘Periodic Table of SWNT’ developed by CNL staff, as well as an excitation-fluorescence spectrum from a mixture of SWNT; each peak in the spectrum corresponds to one unique type of nanotube.

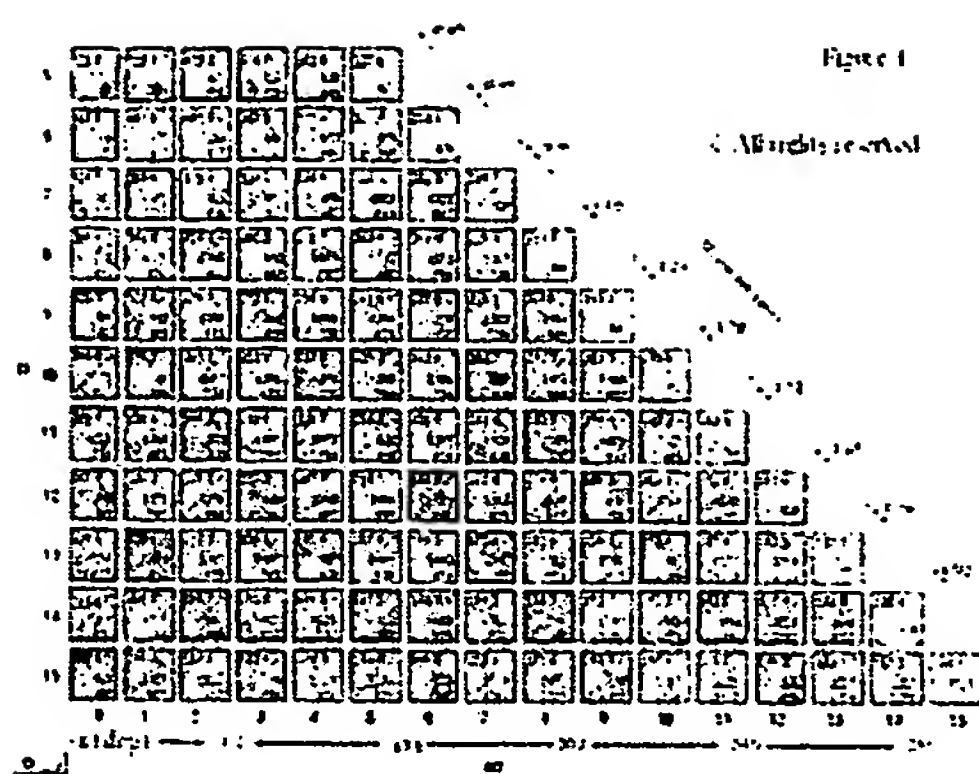
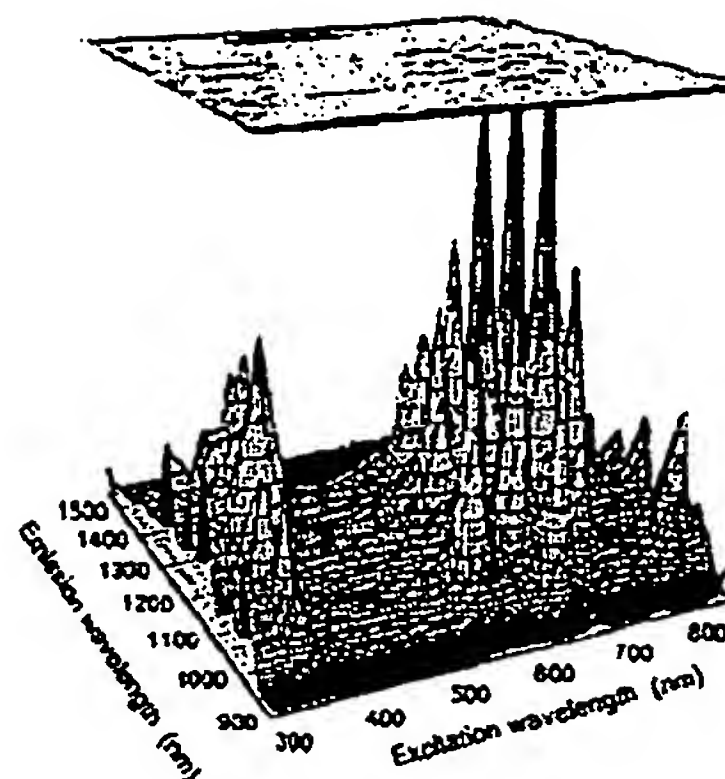


Figure 1

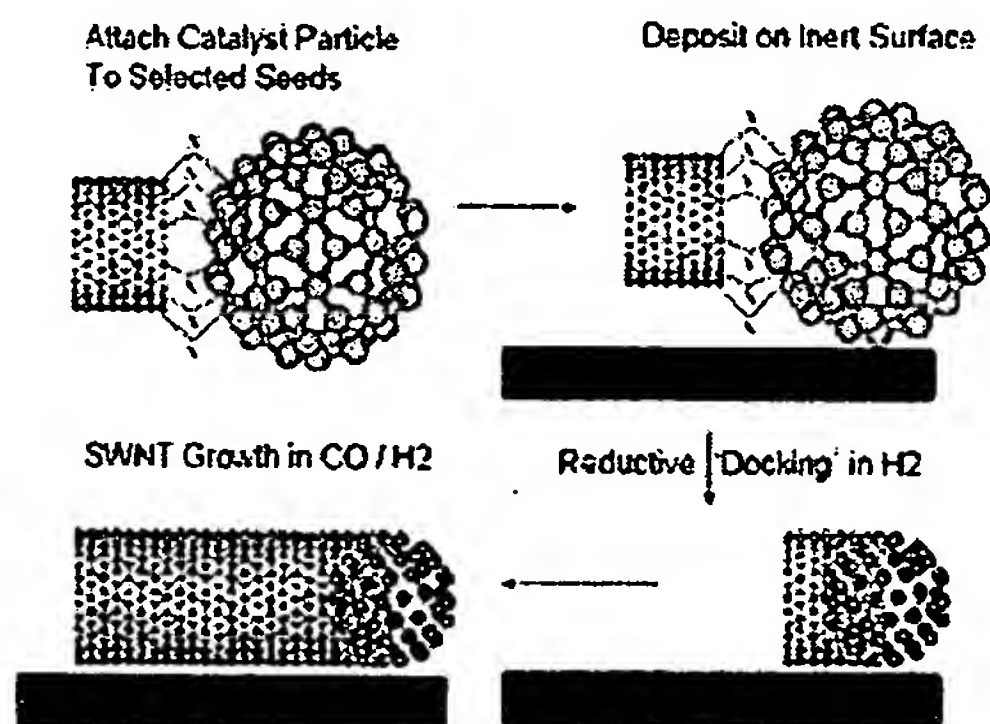
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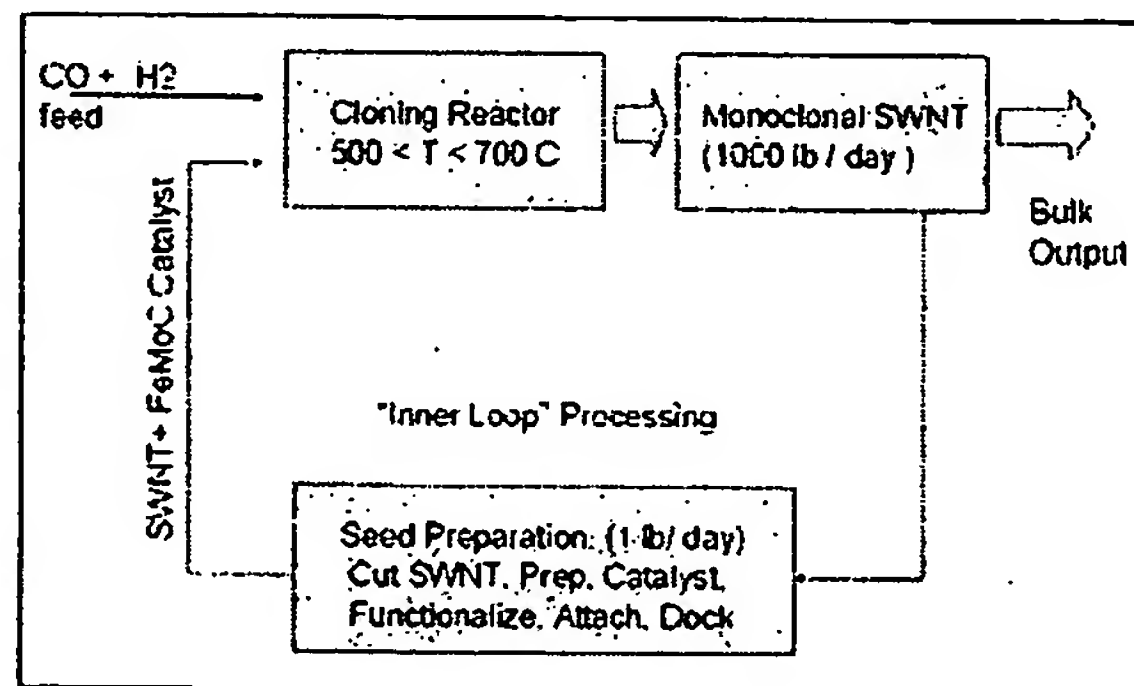
In This (n,m) SNWT Table, Blue = Truly Metallic (Armchair),  
Green = Semiconductors (Chiral), Yellow = Semi-Metals.

Each Peak Is Unique To A Particular SWNT Type

**Cloning.** A key CNL innovation that will enable type-specific, low-cost production is 'Cloning'. By separating and completely controlling the nucleation and growth cycles, we expect that this technology will eventually enable ton-level production at roughly \$30 per pound. The key conceptual break-through in cloning is, for the first time ever, totally separating the nucleation and the growth of carbon nanotubes. As described above, nucleation is random, resulting in several by-product channels and degrading yield. Moreover, and as we shall see, more importantly for the AQW program, a mixture of SWNT types are produced from spontaneous nucleation and growth in the same chamber. Fortunately, we have demonstrated that nucleation from the vapor phase only occurs at temperatures over 900°C, whereas the fundamental growth process can proceed at temperatures as low as 500°C. To run at lower temperatures, we have to deliberately provide both pre-formed catalysts as well as 'starter tube' templates for growth. The cloning concept and reactor/process schematic appear in the following figure.



SWNT Seed Preparation Scheme



BuckyTube Cloning Production Scheme

Since production from clonal seeds will proceed at moderate temperatures and with high purity, we expect that the cost and complexity of the reactor will be minimized, and the throughput and cost of SWNT production will improve dramatically. Two key unit processes that enable success in cloning are a) cutting SWNT to short regular lengths, and b) viable catalyst production and attachment pathways.

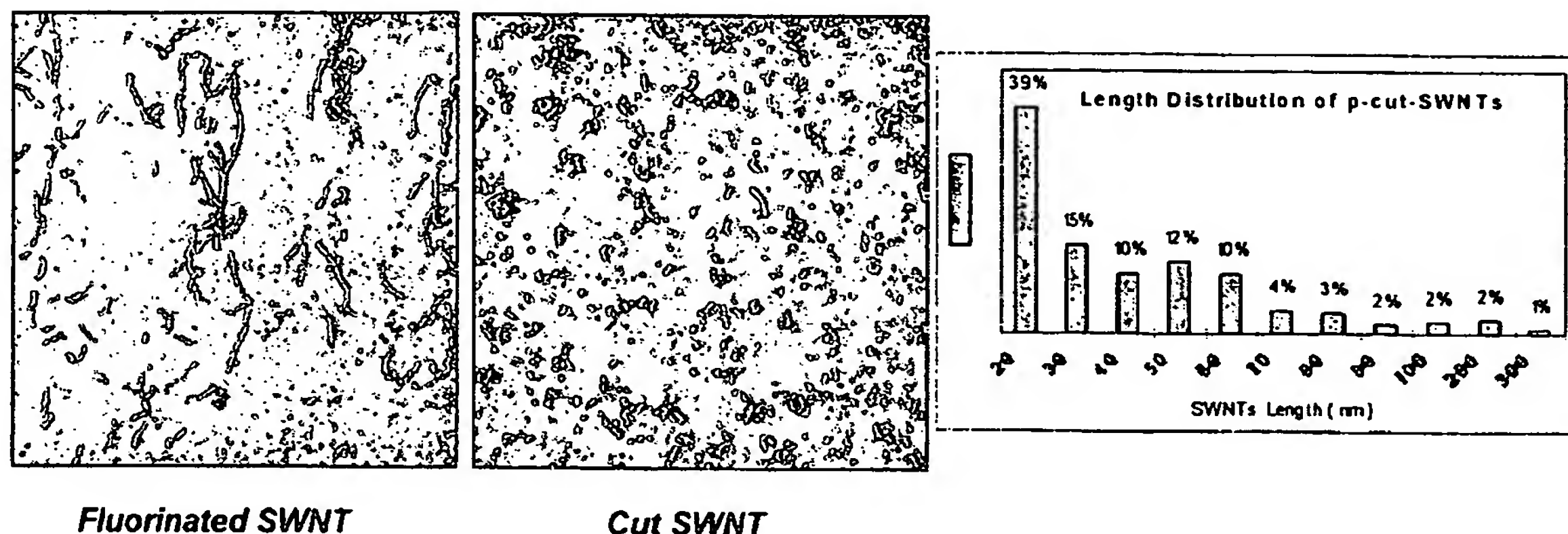
**SWNT Cutting.** Efficient SWNT cutting processes are particularly needed to achieve 'gain' in a cloning reactor. Cutting processes are also needed for a number of SWNT applications, e.g. nanoelectronics and block-copolymer composites. While the SWNT structure is normally almost impregnable, it is susceptible cutting and defect formation under certain extreme conditions. For instance, we have encouraging initial results on cutting via aggregates of chemisorbed electronegative atoms, especially fluorine and oxygen. These are delivered as di-fluorine [11] and ozone, respectively. While the mechanism is not clearly understood, it appears that initial adatoms 'direct' additional chemisorption at adjacent sites, resulting in clusters of fluorine or oxygen. Upon thermolysis, these clusters, or bands



fluorinated SWNT

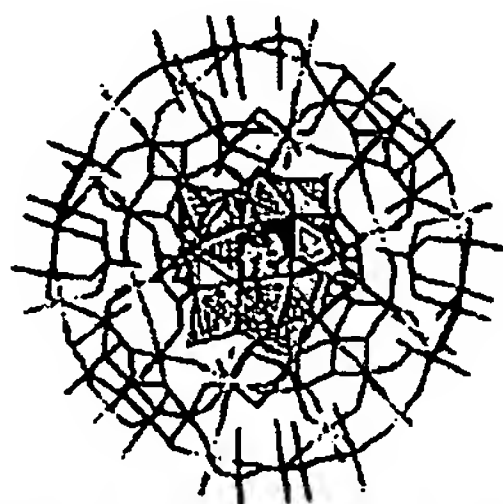


(shown in the adjacent figure), react with the nanotube generating  $\text{CF}_2$  and  $\text{CF}_4$  or  $\text{CO}$  and  $\text{CO}_2$ , respectively. Preliminary AFM results of cutting SWNT with fluorine are shown below, along with size statistics:



This two-step defect-cut process can be conceptually generalized. Thus, we have begun to explore radiolytic means (e.g. energetic electrons, photons and ions) means to produce the initial defects, with a particular focus on 3 MeV electron beam processing. This is a routine and relatively inexpensive industrial process. While it is known that electrons with kinetic energy over 87 KeV can directly remove carbon atoms from SWNT, the cross section is rather low. We hope to increase defect efficiency via 'chemical amplification' by irradiating in an environment that can produce energetic halogen (e.g. F, Cl) or chalcogenide (e.g. O, S) atoms adjacent to the SWNT. This takes advantage of the fact that extensive ionization and excitation occur along the electron track. The chemically active environment is achieved by intercalating SWNT ropes prior to irradiation (e.g.  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{SO}_4$ , etc.) Radiolytic excited oxygen should attack SWNT sidewalls readily, as this is a known process in low-pressure plasma systems. We will then exploit these defects by thermolysis and/or chemical oxidation, as with Pirana etch, to complete the cutting process.

**Catalyst Attachment.** The second critical 'inner loop' step is catalyst synthesis and attachment. We have a veritable arsenal of viable approaches for rational process design here, based upon known surfactant-mediated metal nanoparticle condensations, coupled with verified SWNT end functionalization chemistries [15] to bring the cut tubes and catalyst particles into contact with each other. However, we have fortuitously discovered what is likely an optimal path based on self-assembled Keplerate clusters, and natural coordination chemistry linking these to oxidatively cut nanotubes. Keplerates are self-assembling quasi-spherical clusters of mixed metal oxides. Among this large family of compounds is one that we lovingly call 'FeMoC' (Fe for Iron, Mo for Molybdenum and C for Cluster), shown schematically below [12]. FeMoC is comprised of an outer icosahedral shell containing both Mo and Fe ( $\text{H}_4\text{Mo}_{72}\text{Fe}_{30}(\text{CH}_3\text{COO})_{15}\text{O}_{254}(\text{H}_2\text{O})_{98}$ ) and an inner Mo cluster ( $\text{H}_x\text{PMo}_{12}\text{O}_{40}$ ). All told, the cluster contains 114 transition metal atoms and it is 2.1 nm in diameter in its native oxidized state. The cluster has already been demonstrated to reduce to an effective nanotube production catalyst under SWNT growth conditions [13, 14]. This is a chemically perfect and consistent reagent for SWNT catalytic growth. The material is not expensive, and we can already produce FeMoC in gram quantities with high yield. Fortune smiles further in that FeMoC is readily soluble in common solvents like ethanol, and its sphere of coordinated water molecules can be readily displaced by the poly-carboxylate groups native to the ends of oxidatively cut SWNT. We are currently working on a demonstration of the cloning process; the figure below shows an AFM of self-assembled nanotubes-FeMoC units sitting on an HOPG surface.



FeMoC: An Ideal And Affordable Cloning Catalyst



Cut-SWNT and FeMoC Self-Assemble In Solution (AFM Image)

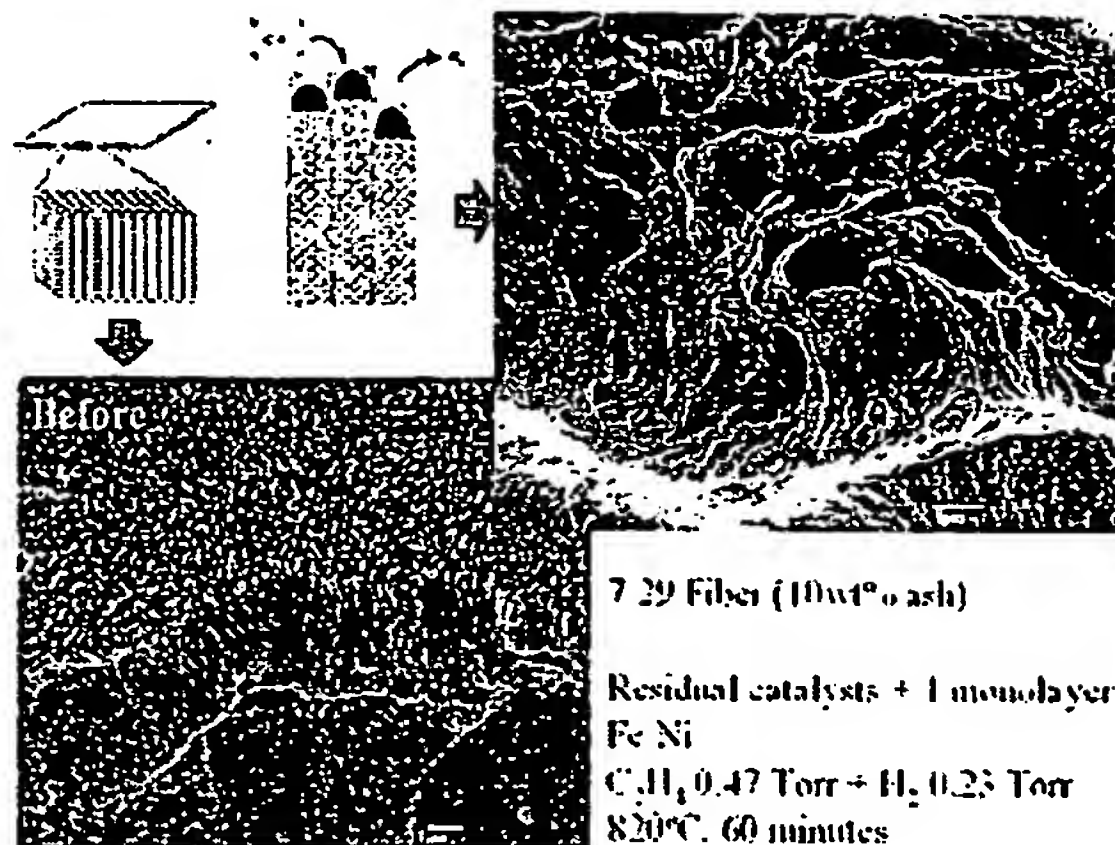


After we choose a particular cutting/catalyst/growth process, we will go about developing a new generation of optimized Cloning Reactors. There are two fairly obvious approaches a) HiPco-like using injected seeds, and b) supported growth based on seeds sitting on sacrificial high-surface area refractory powders. The latter could be based upon either fixed- or fluidized-bed designs; both are well-known industrial technologies.

**Continued Growth & Membranes.** An additional approach to be explored would grow conductive fibers in near net-shape as a film or aligned membrane. This is similar to what we call 'continued growth'. We have in-hand some results indicating that this is indeed possible. The SEM images (figure, right) show partial continued growth from a neat SWNT fiber. The material was composed of mixed HiPco SWNT. The re-nucleation efficiency is currently rather low with evaporated thin metallic catalyst films, but these results demonstrate conceptual feasibility of continued growth.

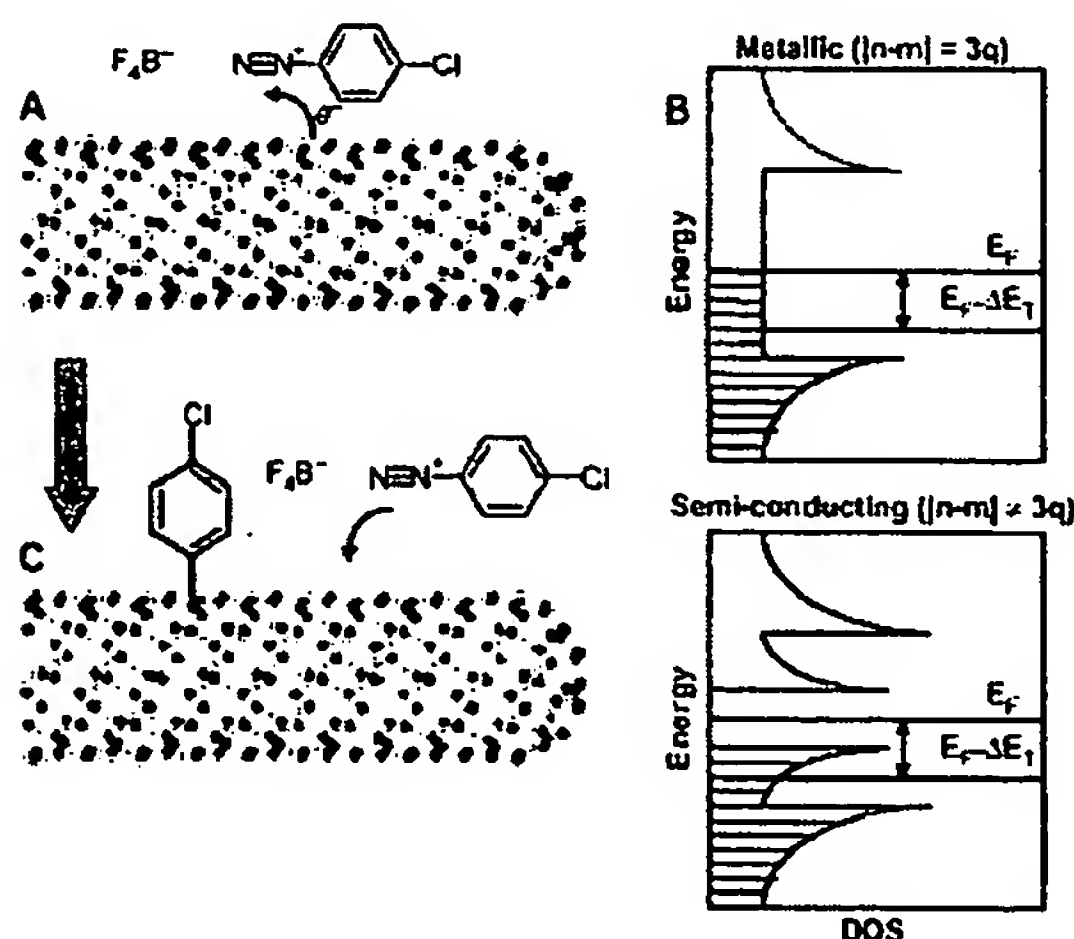
CNL researchers have also recently produced self-assembled monolayers (SAM) of FeMoC on various substrates, as well as progress towards SAMs of SWNT with attached nanotubes. Such assemblies will be explored as starting materials for clonally pure aligned SWNT membranes and structures.

The Continued Growth from a "Bed-of-Nails" like substrate

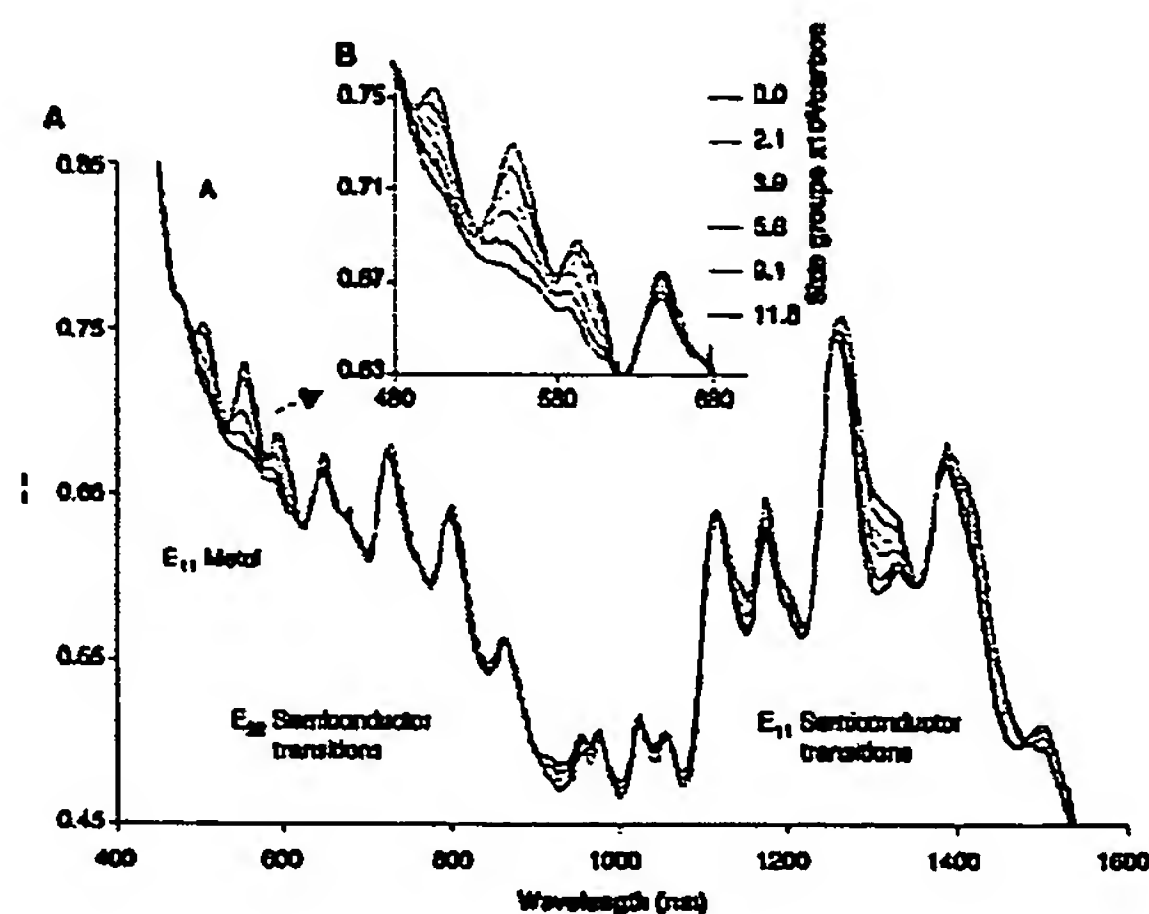


Partial Continued Growth of Neat SWNT Fibers

**SWNT Type (n,m) Sorting.** We will initially require milligram quantities of selected metallic tubes as feedstocks for cloning production. After experimentally surveying the bulk conductive characteristics of several chosen candidates, we expect to concentrate SWNT and AQW production efforts on the single best type. Using mixed feedstocks from existing HiPco production, we plan to extract selected SWNT by a combination of chromatographic techniques [31] and selective chemistries, both proven [15] and novel. For instance, we have recently demonstrated that metallic SWNT can be preferentially side-wall functionalized with selective free-radical adducts [15] (figure below, left). This process enables simple and efficient separation of metallic from semiconducting tubes in a surfactant-stabilized aqueous solution. The figure below, right shows the progressive functionalization of metallic tubes, as observed by UV-Visible absorption spectroscopy.



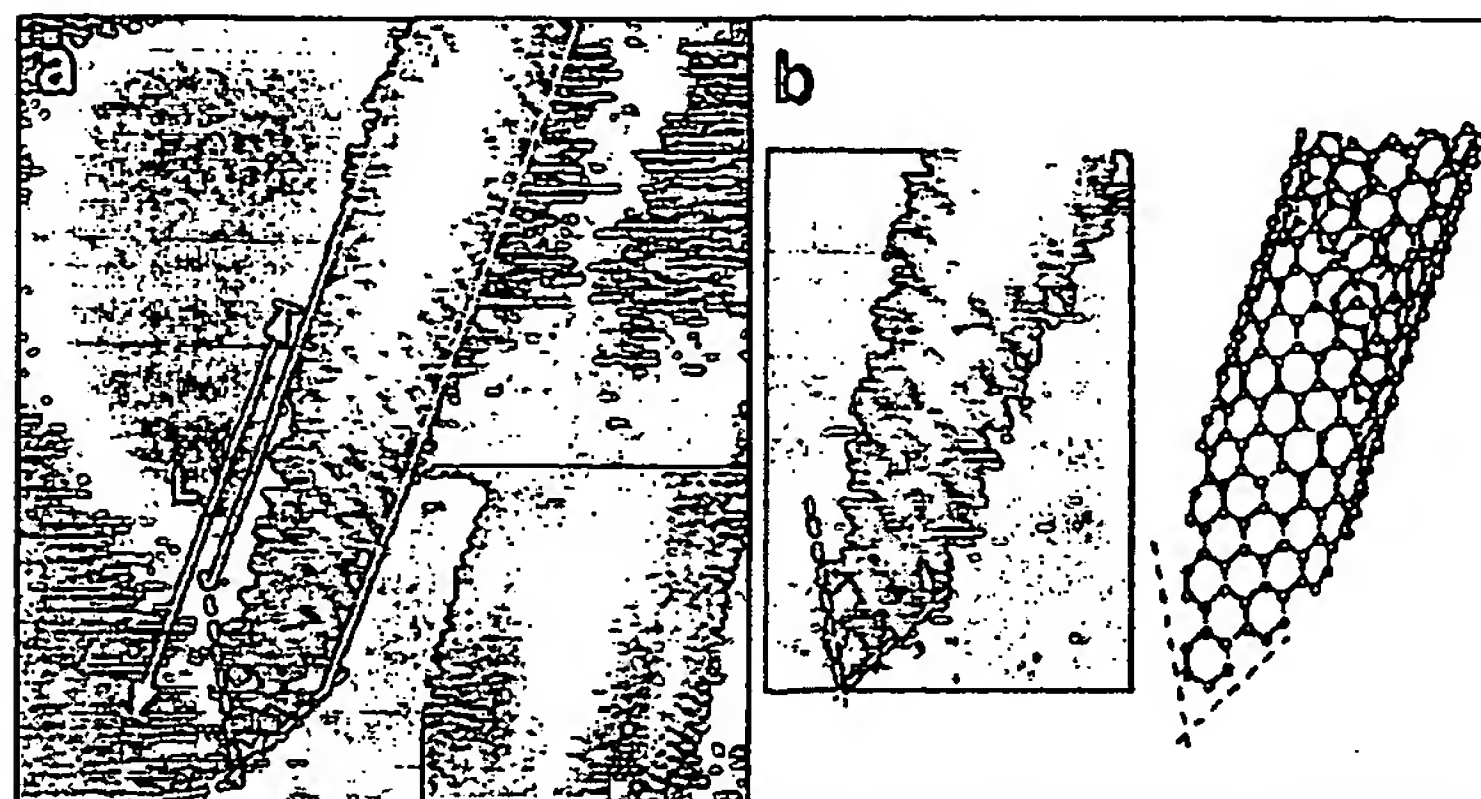
Selective Functionalization Separates SWNT By Class. [15]



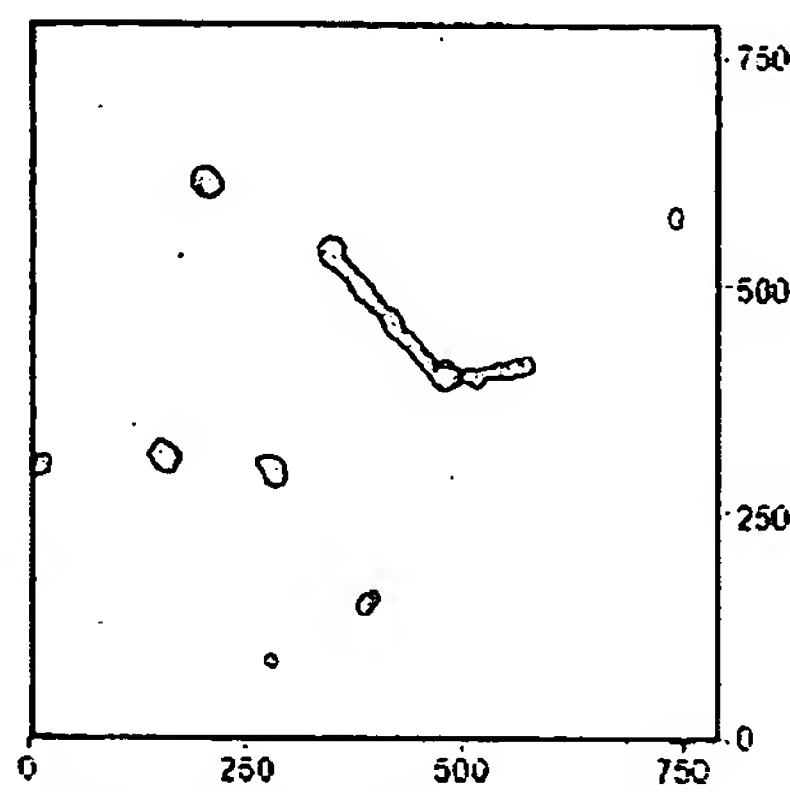
Type-Selection Can Be Monitored In Real-Time. [15]

More specific separations will be based upon the unique end-chemistry of oxidatively etched nanotubes. As Lieber [20] recently observed, chemical oxidation of SWNT preferentially exposes all-armchair edges at the ends of the tubes (see figure below, left). We know from our earlier work on "fullerene pipes" [32], that the ends of

etched SWNT are decorated with carboxylic acid groups. Indeed, these form the basis for end-functionalization chemistries that support attachment to metal particles. In the 'seven minutes to three' AFM image (below, right), shortened nanotubes were attached to gold particles using thiol terminated alkyl chains attached to SWNT via such carboxylic groups.



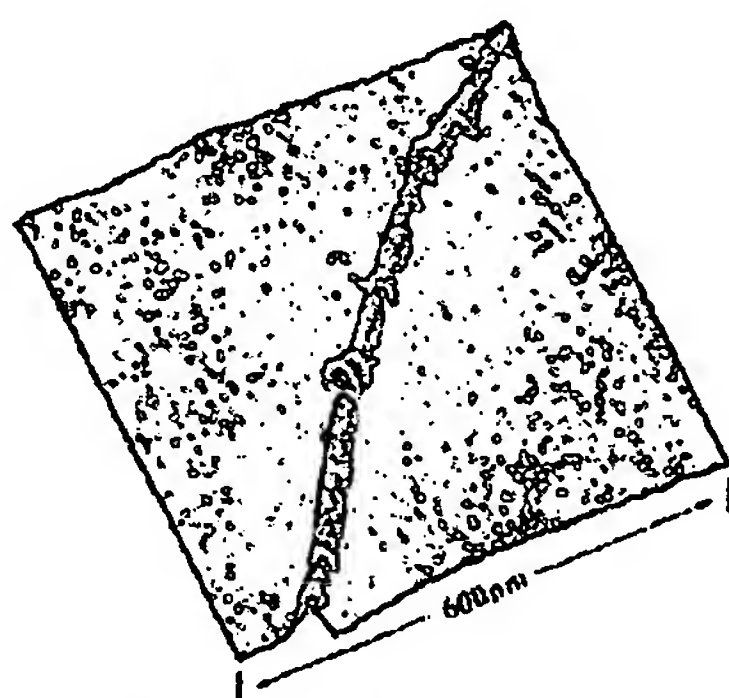
Distinct (n,m) values lead to unique end chemistries and geometries. [20]



End chemistries attach metal particles. [32]

As such, distinct SWNT (n,m) types have unique chemical signatures determined by their chirality and diameter – both in terms of the number of carboxylic acid groups, as well as their spatial extent and geometric arrangement. For instance, the minimum number of acids would be expected on small diameter 'armchair' tubes – the kind we plan to use for building quantum wire and cable. Earlier work [31] defined a general approach to separating tubes based on differential drag in capillary electrophoresis of surfactant-suspended SWNT, even though complete separation was confounded at the time by a multiplicity of lengths and charge-masking effects of the surfactants. Recent CNL advances in SWNT sidewall functionalization by a number of routes now generate individualized SWNT completely soluble in both organic and aqueous media. By combining these methods, and simplifying their implementation using short segments of cut tubes (see above), we expect to be able to obtain pure samples of selected SWNT for amplification and AQW production.

A pair of highly specific and novel separation methods, based on antibody affinity and photo-ablation, will also be explored. It has been already demonstrated that fullerene-specific antibodies [33] can be produced and attached to SWNT [34], as shown in the AFM image below, left. It is reasonable therefore that we should be able to develop specific antibodies for the etched ends of each (n,m) type of SWNT and use tethered versions of these for total separation in affinity chromatography columns. The second approach will exploit the meta-stable nature of surfactant-suspended SWNT micelles [15] (figure below, right). Here we will utilize photo absorption features specific to particular (n,m) and SWNT classes to de-solvate and precipitate SWNT from suspended mixtures. For example a tunable pulsed IR laser would be used to dynamically and selectively heat SWNT with a particular IR feature (radial breathing mode absorption); these would then flocculate from the aqueous suspension. Similarly one could use a pulsed broadband far-infrared source to selectively unwrap and precipitate metallic tubes. Centrifugation (used to form the original surfactant 'decants') would then be used to separate SWNT populations of interest.



Fullerene-specific antibodies (bumps) bind to SWNT. [34]

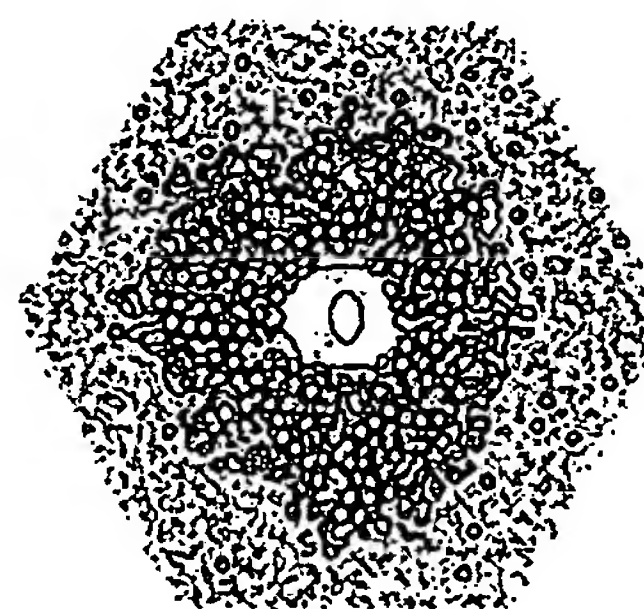
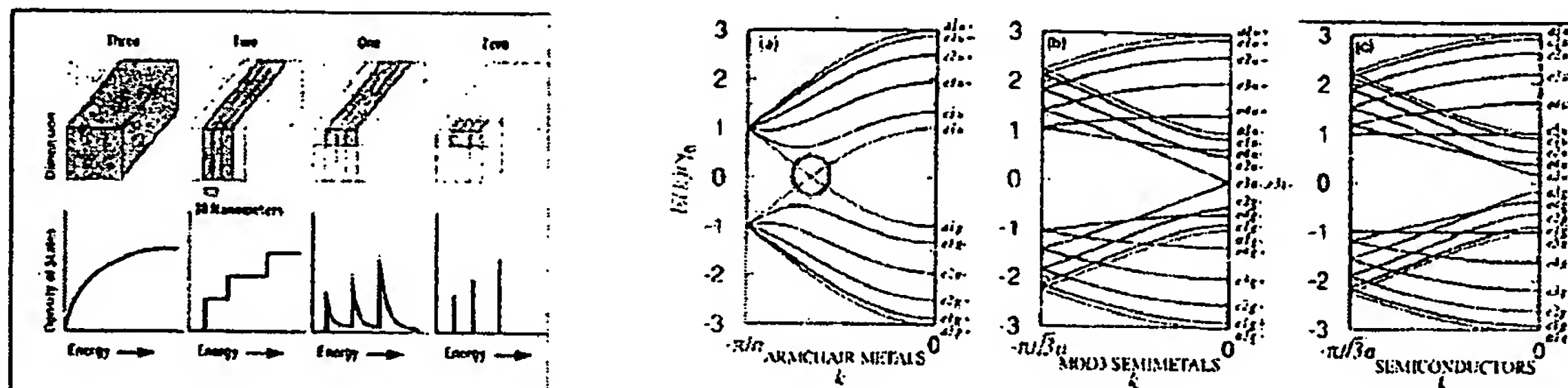


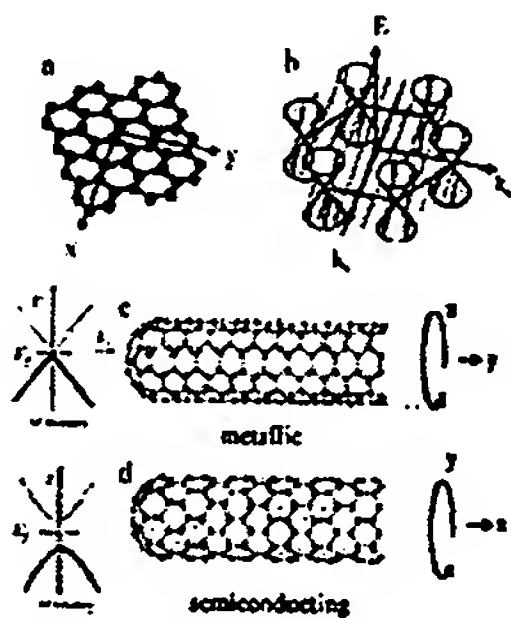
Photo-labile surfactants enable SWNT separations. [15]

**Armchair Quantum Wire.** Recent research efforts on individual Single-Wall Carbon NanoTubes (SWNT) have demonstrated as fact the much-heralded expectation that certain SWNT types have the highest known carrier mobilities and current densities approaching  $10^{10}$  A-cm<sup>-2</sup> [16, 17]. These results, combined with less famous experimental and computational results involving electron-phonon interactions, carrier lifetimes and mean free paths, we can now realize a solid opportunity to develop revolutionary macro-scale electrical components based on SWNT fibers and cable assemblies. Indeed it is reasonable to expect that a proper development and integration of specific-type SWNT, high-transmission contacts and fiber processing technology could yield conductors with over two orders of magnitude improvement over copper in current carrying capacity per unit weight. This approaches the practical range of high temperature superconductor engineering – about 100x the current density of copper – but without cryogenics.

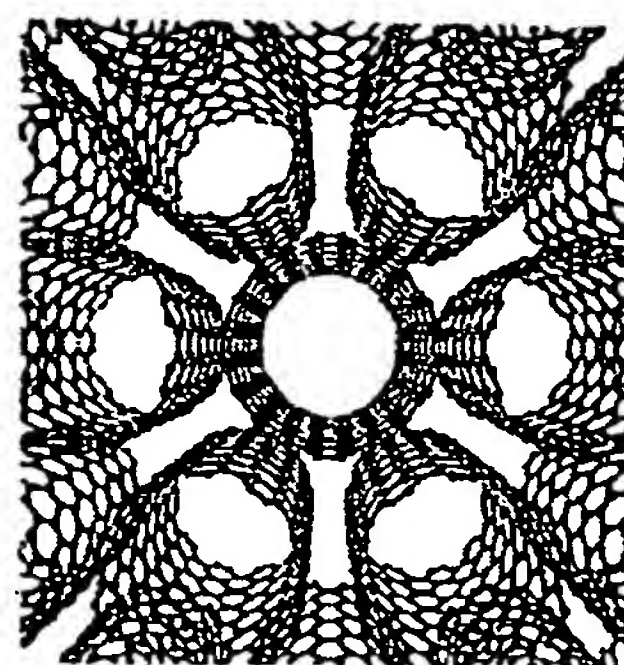
To describe how we will do this and why we are confident of a positive result, we should review the electronic properties of SWNT. Since SWNT are uni-dimensional, their band structures differ from familiar bulk materials in important ways. With decreased dimensionality, energy levels become increasingly quantized, meaning that the number of allowed states for an electron (or phonon...) is reduced (see figure below, left). Calculated band structures for the three generic types of ideal, isolated SWNT are shown below (right) [1].



For bulk conductance, plainly we are interested in the metallic tubes. Semi-metals have a very small band-gap (on the order of  $kT$ ), and so are conductive at room temperature, but have lower conductivity than true metals, so our interest is focused on the latter – the Armchair tubes – hence the Armchair Quantum Wire.



Local Geometry Defines Electronic Structure



Perspective View of AQCW Bundle of (10,10) SWNT

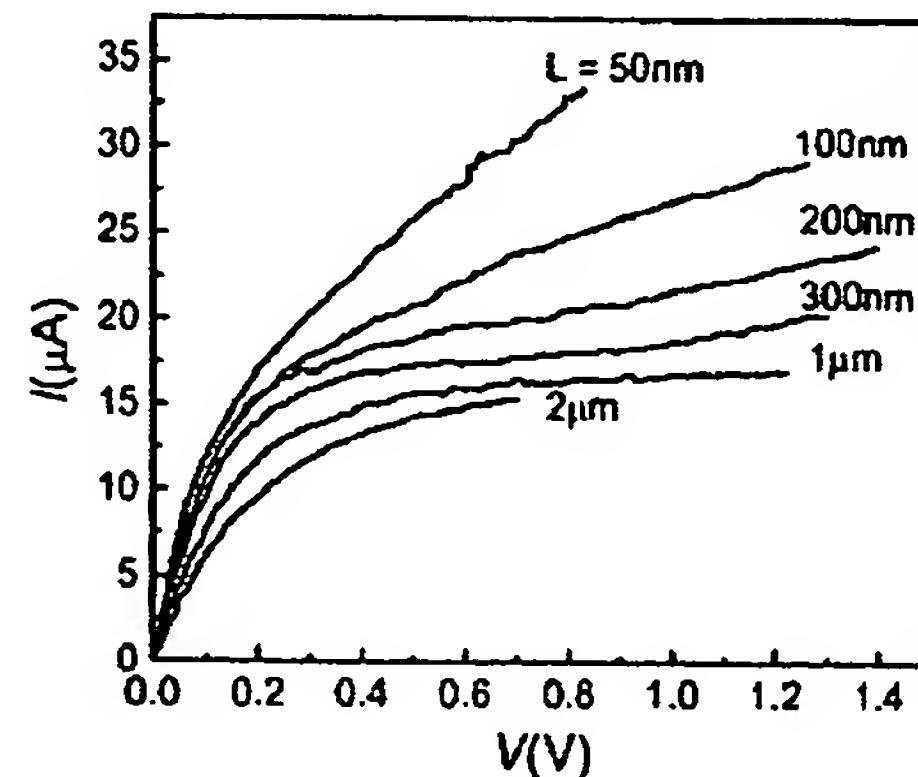
SWNT are uni-dimensional conductors with diameters around one nanometer, they behave as individual quantum wires. Thus, conduction from contact to tube to contact has to be treated as a unified quantum event. Essentially, to get conduction have to match the tube's wave function to those of the contacts – contact transmission becomes important, as well as the number of allowed states or bands, in the conductor. For metallic tubes (of either kind), the resistivity with four sub-bands in the incoherent limit is given by Landauer's equation:

$$R = \left( \frac{h}{4e^2 T} \right) \cdot L_{wire} \left( \frac{1}{\lambda_e} + \frac{1}{\lambda_{ac}} + \frac{1}{\lambda_{opt}} \right)$$



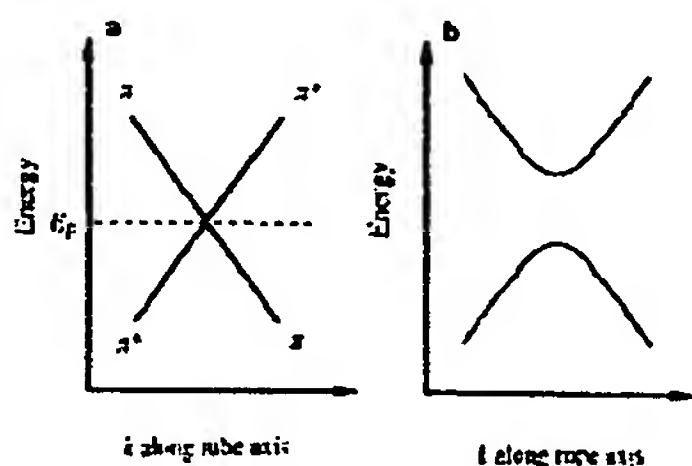
where  $\hbar/4e^2 = 6.5 \text{ k}\Omega$ ,  $T$  is the transmission of the metal contacts to the nanotube,  $L$  the length of the tube, and the  $\lambda$ s the mean free paths for scattering by impurities (elastic scattering), and acoustic and optical phonons (inelastic scattering), respectively. The collection of  $1/\lambda$  terms is manifested as the mean free path of the electron before a back-scattering event. Nominally,  $\lambda_e$  is a few microns (due to impurities/adsorbates),  $\lambda_{ac}$  is long, and  $\lambda_{opt}$  depends on the applied voltage. In a high energy ballistic regime where the energy of the electrons exceeds  $\sim 0.2 \text{ eV}$ , excitation of optical phonons becomes possible, and reduces the mean free path of about 20 nanometers.

Plainly, this is a topic of some interest due to the importance of quantum wire behavior in SWNT device electronics. Short, individual tubes have been studied rather extensively, though by no means exhaustively or perfectly. Key results have been reported by McEuen [16,17], that bear out the basic features of the above prediction. Indeed, with good contacts, a very attractive effective resistance was found in the low field regime –  $4 \text{ k}\Omega / \mu\text{m}$ . This was mediated by interaction with low energy (acoustic) phonons. At high fields, optical phonon interactions become very pronounced and effectively clamp the maximum current through the tube to about  $25 \mu\text{A}$ . The figure at right shows i-V curves measured at several positions along a given nanotube. This exciting result does not represent the ultimate for SWNT. The exact tube type was not determined (it could have been either armchair or mod3). Substrate interactions, bends and impurities all existed, but could not be eliminated from the result.

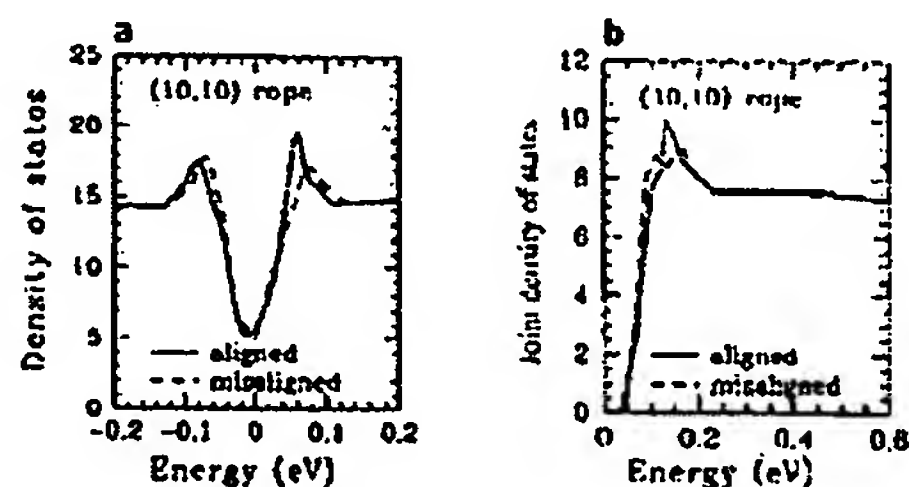


Still, the results bode extremely well for AQW. The inferred mean free path was  $1.6 \mu\text{m}$ . Given the measured diameter of the test article,  $1.8 \text{ nm}$ , the equivalent bulk resistivity of an assembly of such tubes would be about 2.5 times better than copper, with  $\rho \approx 0.7 \mu\Omega\text{-cm}$ . Normalized to the density of the materials (SWNT vs. Cu), the conductivity-weight performance would be about 20 times better than copper.

Our goal is not individual tubes, but vast assemblies of armchair SWNT packed into hexagonal arrays. Comprehensive theory for this situation is lacking. Calculations on representative structures have been performed, however, and the results are intriguing. Louie, Cohen, et al., [19] have published interesting results predicting the appearance of a "micro-gap" in a bundle of (10,10) tubes due to reduced radial symmetry in a given tube's local environment. Indeed, in some elegant work by Lieber, et al. [20], electron Density of States (DOS) measurements of a metallic tube in a bundle appear to display such a feature.



Bundling Could Create A "Micro-Gap" [19]

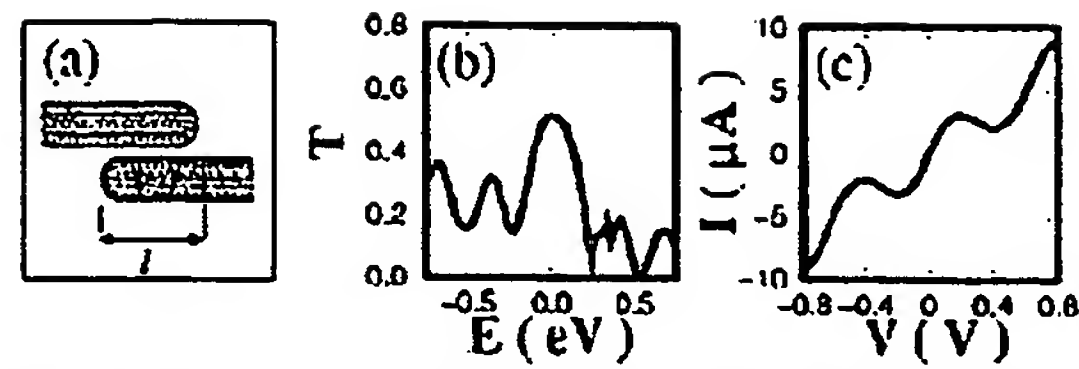


Calculated Micro-Gap DOS In (10,10) Bundles [19]

What exactly this might mean for a real conductor is not at all clear. A significant reduction in DOS at the Fermi level could reduce conductivity. However, the phonon DOS will undergo similar changes [21, 22, 23], thereby decreasing the ability of acoustic phonons to impede electron flow. These are competing effects that will have to be investigated experimentally.



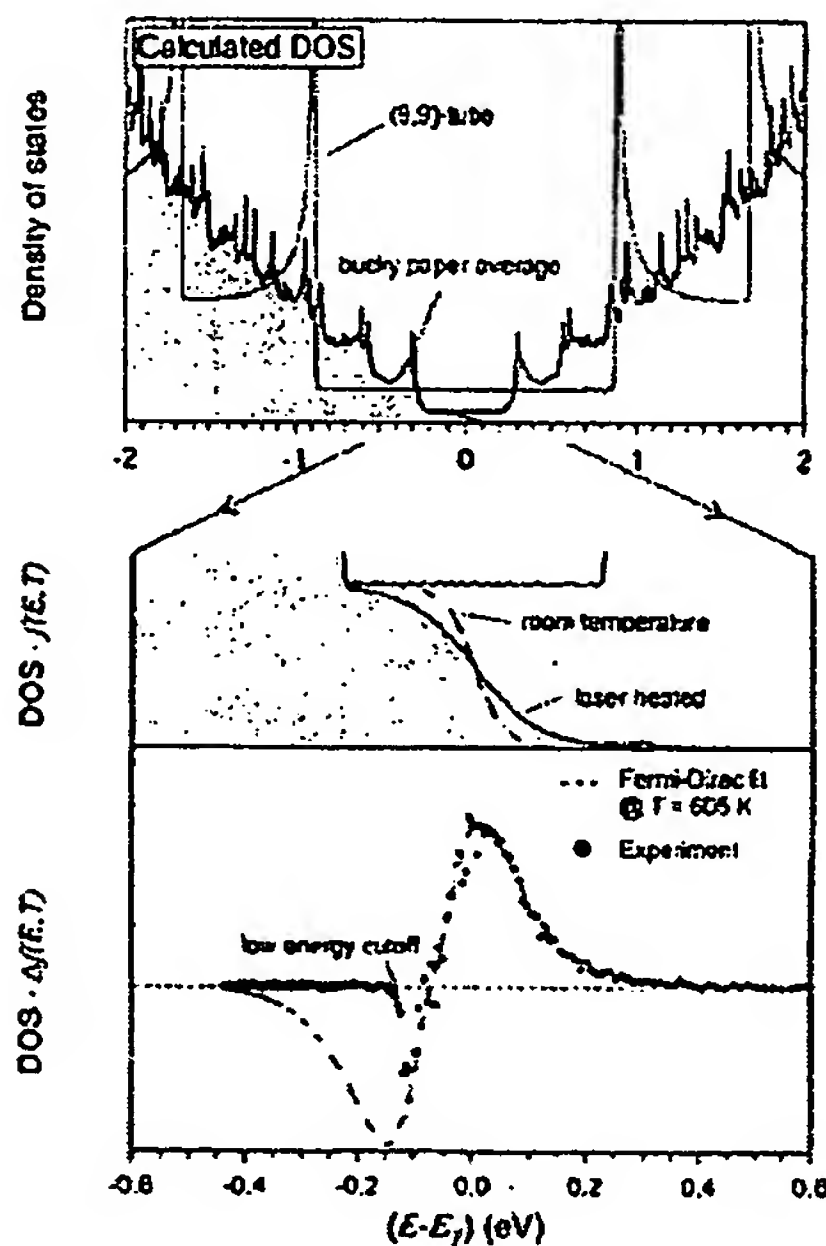
As mentioned in the introduction, maintaining clonal purity in Armchair Quantum Wire will be critical to maintaining high conductivity in bulk assemblies. This will enable us to take advantage of resonant quantum tunneling effects between adjacent tubes of identical type. This effect has been modeled by Buldum and Lu [26].



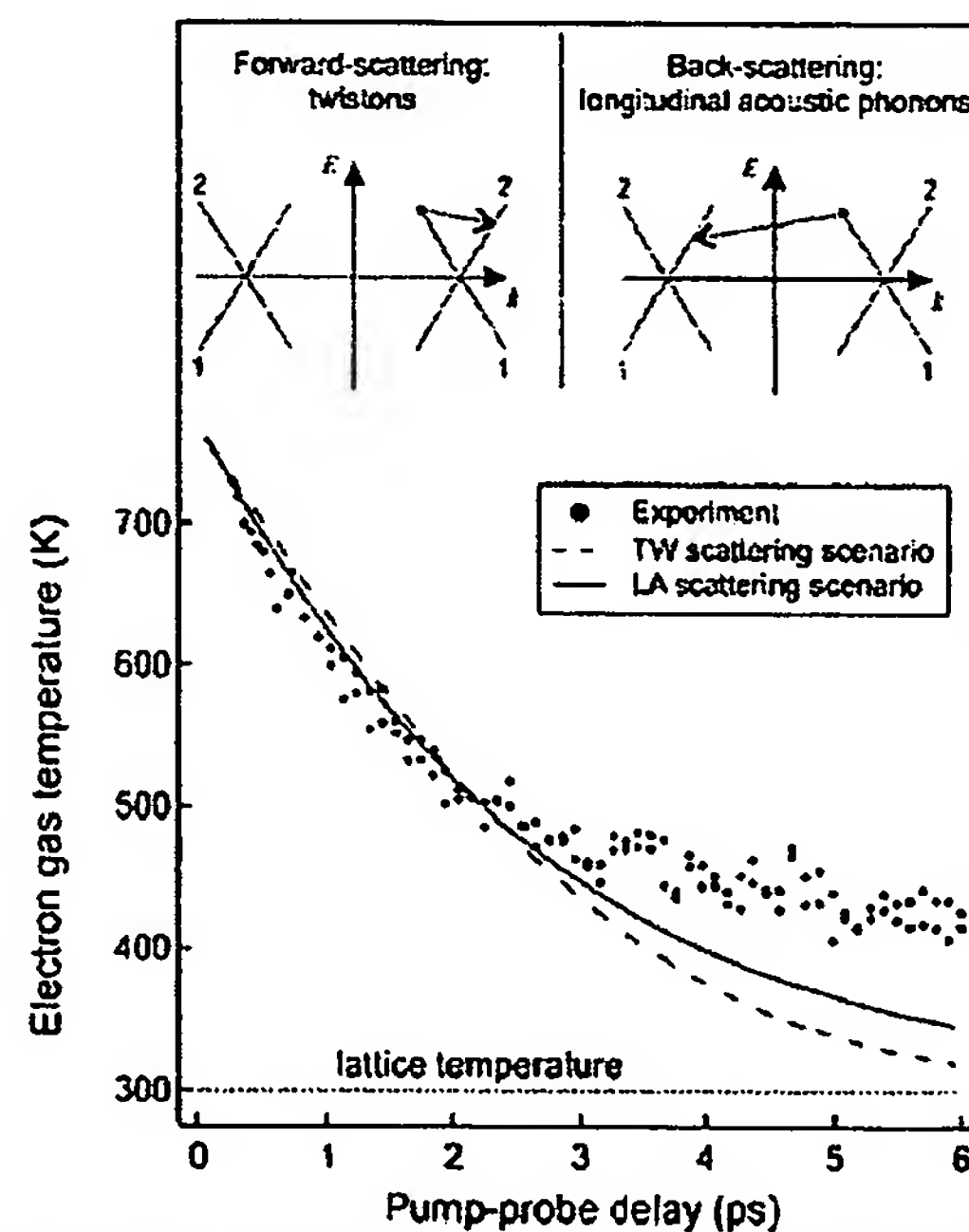
Tube-Tube Resonant Quantum Tunneling Preserves High Conductivity In The ArmChair Quantum Wire [26].

Their key results are shown above, right, and demonstrate that the quantum transmission coefficient (per Landauer) will be better than 0.5 in the energy range of interest, as long as the overlap between adjacent tubes is on the order of 100 nm. This essentially defeats reflection at the ends of tubes of finite length. With basic SWNT elements over 10 microns in length, we would expect the macroscopic resistivity of AQW to be not more than twice that of wire constructed of infinitely long tubes.

In an important report by Hertel, *et al.* [24], many of these issues can be resolved. Using a buckypaper sample produced at Rice, Hertel measured the mean free path of electrons in ropes of mixed SWNT. The ropes in buckypaper are very nearly perfect hexagonal arrays of very high quality SWNT. Thus, the structure is microscopically very similar to our proposed Quantum Wire. Furthermore, the clever nature of the experiment eliminates terminal contact transmission effects, and includes the effects of finite length nanotubes in bundles of macroscopic lengths.



Laser Excitation Pumps SWNT Electron Temperature [24]



TOF Photo-Ionization Probes Electron Cooling Rate [24]

Specifically, Hertel's clever pump-probe experiment perturbs the electron energy distribution (temperature) with one photon, and then measures the temperature as a function of time using a second ionizing photon. The electron's level (temperature) is inferred from the energy of the ejected electron by time-of-flight. Hertel's conclusion is that the electron's mean free path is about 15 microns in this mixture – an order of magnitude greater than McEuen's result using isolated SWNT. Since a) the sample contained only a fraction of metallic SWNT and b) only a fraction of these were Armchairs, and c) the SWNT nanotubes in the sample were only about one micron in length, we might take this as a lower bound on the ultimate performance of Armchair Quantum Wire. Interestingly, the electrons cooled more slowly (*i.e.* had less loss to phonons) than current theory predicts – this may be a manifestation of efficient lateral tube-tube tunneling, per computational predictions [25, 26]. Plainly, such results behoove us to explore and model this arrangement in more detail during the proposed program.

If Quantum Wires perform at least this well on the macro-scale, their basic conductivity would be about 25 times that of copper, and normalized to mass, AQW would provide two orders of magnitude advantage over copper. Additional optimizations may be possible as well. For instance, modeling results by Anantram [27, 28, 29, 30] hint that larger tubes will have more useable sub-bands, and that tunneling contacts may increase transmission factors by a factor of two over the Landauer norm.

There will be, of course, many degrees of freedom that will have to be explored, characterized and controlled in the AQW program to realize the maximum possible performance of SWNT aggregates in large conductors. Chiefly, we will have to master production of specific types of SWNT on large scales, and develop processing methods for forming large almost-perfect arrays without degrading the purity of the material. Additional work will be required on optimizing contact metallization along with optimal SWNT type selection. All of these development activities will need to be supported by an integrated modeling effort, as well. Though challenging, a strong and focused Quantum Wire program should deliver a truly revolutionary product while simultaneously enabling a new class of affordable materials and technologies.

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## Constructive Plan

### Task 1 Cloning Process Development.

Rationale	While the needs for large amounts of pure, type-selected SWNT are clear, current SWNT production technology has several key limitations. Most importantly, combining catalyst formation, nucleation and growth at high temperatures results in high levels of impurities and by-products while complicating reactor design and construction. Current conditions also allow for promiscuous nucleation of multiple SWNT types, though limited control of type distributions has been demonstrated.
Approach	Via 'cloning', we shall rationally separate critical SWNT production steps, especially those of catalyst formation and tube growth. Promiscuous nucleation will be avoided entirely by operating at lower temperatures and using seeds produced from small quantities of class- and type-selected SWNT feedstock. Seeds will be made by physi-chemical cutting of selected SWNT. Several cutting approaches have been preliminarily demonstrated; these will be further explored and the optimal process developed. Key SWNT organic and organo-metallic functionalization chemistries for SWNT are known; routes for attaching pre-formed catalyst particles to cut tubes will be explored and the optimal pathway further developed. Known methods exist for rationally forming nanometer-scale metal and alloy particles under mild conditions; these include self-assembled Keplerates and surfactant-stabilized condensates of metal carbonyls. These methods will be explored and the optimal system developed. Micro-scale separation of specific SWNT are sufficient for the program needs; we shall explore and extend prior efforts based on physical, chemical and electro-dynamic methods to produce a catalog of feedstocks for cloning production. We shall initially demonstrate, characterize and integrate the several process steps using individually observable seeds immobilized on well-defined surfaces. Later stages will involve micro- and bench scale production of type-selected SWNT. Technical results will be transferred continually to Task 3. for scaling and production planning.
Benefits	<ol style="list-style-type: none"><li>1. Process technology for significantly increasing purity of as-grown SWNT.</li><li>2. Process technology for manufacturing single-type selected SWNT.</li><li>3. Process technology for low cost, high-volume SWNT production.</li></ol>
Sub-Tasks	<ol style="list-style-type: none"><li>1. Develop cloning catalyst production to 30-gram levels; prove kilo feasibility.</li><li>2. Develop SWNT cutting to kilo levels; prove ton feasibility.</li><li>3. Develop SWNT functionalization to kilo levels; prove ton feasibility.</li><li>4. Develop attach process to 30-gram levels; prove kilo feasibility.</li><li>5. Develop class-specific SWNT separations to 30-gram level.</li><li>6. Develop type-specific SWNT separations to gram level.</li><li>7. Demonstrate full-cycle cloning on well-defined surfaces.</li><li>8. Develop supported seed methodology to kilo level; prove ton feasibility.</li><li>9. Produce and deliver class- and type-selected seeds to other Tasks.</li><li>10. Model and document technology for transfer to commercial operations.</li></ol>

### Task 2. Ordered Growth & Template Assembly.

Rationale	Current SWNT production technology based upon gas-phase precipitation in a flow-through reactor results in geometrically disordered growth, which reduces yield and throughput. The resulting fluffy bulk complicates reactor design, impedes continuous production and makes post-processing into shaped articles difficult. Growth from dense well-ordered templates is therefore highly desirable for production scaling. Similarly, continuous growth from solid pre-forms, including membranes, plates, fibers and rods will help speed development of several applications.
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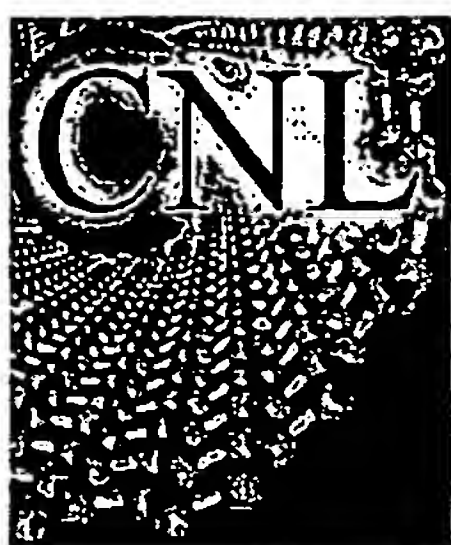
Approach	Ordered substrates will be developed concurrently along two paths – a) performs fabricated from one or more wet-spun SWNT fibers, and b) thin-film templates assembled from SWNT seeds. Well defined catalyst particles and attach chemistries from Task 1 will be employed in this effort. Conceptual feasibility for this approach has been demonstrated using thin-film catalyst layers deposited in high vacuum on cut fiber ends. Larger areas of more complicated geometries will necessitate development of thin film seed templates. Various known phenomena including shear orientation, chemically-directed self-assembly, electrodynamics and electrophoresis will be explored and exploited to develop a general methodology for producing vertically-oriented seed beds. Finally, we shall explore electrostatic and magnetic means for orienting seed-catalyst in the gas phase and dynamically depositing them on the surface of growing SWNT objects, e.g. rods and plates in a medium temperature reactor system.
Benefits	<ol style="list-style-type: none"> <li>1. Improved productivity in flow-through SWNT production reactors.</li> <li>2. Reduced post-processing and handling required for shaped articles.</li> <li>3. Enable near-net-shape production of complex SWNT components.</li> <li>4. Enable tailored SWNT membrane and arrays power &amp; quantum devices.</li> </ol>
Sub-Tasks	<ol style="list-style-type: none"> <li>1. Develop fabrication and pre-prep methods for fiber-based substrates to 1 cm<sup>2</sup>.</li> <li>2. Develop catalyst attach and docking methods for substrates up to 1 cm<sup>2</sup>.</li> <li>3. Develop methods for assembling arrays of seeds on substrates up to cm<sup>2</sup>.</li> <li>4. Develop methods for depositing oriented seeds on articles in-situ.</li> <li>5. Demonstrate continuous growth over 1 cm<sup>2</sup>, prove feasibility for 1 cm x 1 meter.</li> <li>6. Produce, characterize and deliver test articles to Partners and other Projects.</li> <li>5. Model and document process and reactor technology for commercial transfer.</li> </ol>

### Task 3. SWNT Production & Scaling.

Rationale	Various complexities and inefficiencies of current growth technology limits production volumes, necessitates laborious purification and results in high costs. Within current approaches, recent results indicate that some of these issues can be partially ameliorated. New growth and production approaches from Tasks 1 and 2, can be implemented incrementally. Current and planned SWNT research and development requires a continuous flow of working material – at ever increasing volumes and with continually more stringent specificity.
Approach	Our approach to development needs and future capacity is to maintain and incrementally improve current production technology, while simultaneously developing new reactors that exploit advances gained concurrently in Tasks 1 and 2. In-house efforts will extend through bench and laboratory-scale reactor modeling, design, construction, operation and evaluation. Supporting operations for material characterization and purification, if needed, will be developed concurrently. Bulk and specialty material will be delivered to other Program Partners as needed and as available. Technical results of the program will be codified for subsequent commercialization and production.
Benefits	<ol style="list-style-type: none"> <li>1. Continuous and increasing supply of SWNT at monotonically decreasing cost.</li> <li>2. High-purity SWNT production (10x to 100x better than current).</li> <li>3. Type-Selected SWNT for application development.</li> <li>4. Scalable low-cost SWNT production technology for commercialization.</li> </ol>
Sub-Tasks	<ol style="list-style-type: none"> <li>1. SWNT production, purification, characterization &amp; delivery.</li> <li>2. HiPco process variation and improvement.</li> <li>3. Liquid/gas seed injection reactor development.</li> <li>4. Continuous product extraction for gas-phase reactors.</li> <li>4. Fixed-bed reactor for supported seed growth development.</li> <li>5. Fluidized-bed continuous reactor for supported seed growth development.</li> <li>6. Process &amp; reactor modeling and scale-up planning.</li> </ol>

#### Task 4. Armchair Quantum Wire.

Rationale	Experimental results on individual nanotubes indicate current carrying capacities vastly superior to copper. Modeling results indicate that type-matched tubes of finite lengths over 100 nm will enjoy efficient lateral quantum tunneling. Thus, well axially connected quasi-crystalline fibers and cables of same-type metallic SWNT should exhibit extremely high power carrying capacity, along with high mechanical strength and low TCE.
Approach	Using first mixed-metallic, then type-optimized SWNT, CNL staff will initially fabricate small-gage conductors using previously demonstrated methodology based on spinning quasi liquid crystalline SWNT/super-acid mixtures. Post-processing techniques will be evaluated and developed for maximizing alignment, crystallinity and connectivity. Test articles will be fully characterized and compared to expectations developed from computational modeling and predictions. Alternative/enhanced coagulation/crystallization methods will be explored, including electrodynamic crystallization, net-shape continuous growth and fiber-bundle re-crystallization. The most promising of these will be further developed for production of higher-gage quantum cables.
Benefits	<ol style="list-style-type: none"><li>1. Improved strength &amp; weight factors in aerospace signaling systems</li><li>2. Reduced weight in power busses in aerospace and man-portable systems</li><li>3. Reduced weight, size &amp; cost in propulsion motors &amp; motor/generator sets.</li><li>4. Higher reliability, strength &amp; power density for electric grid cabling with zero sag.</li></ol>
Sub-Tasks	<ol style="list-style-type: none"><li>1. Super-Acid Spinning for SWNT Quantum Conductors (AQW).</li><li>2. Computational Modeling of SWNT Conductor Systems.</li><li>3. Characterization &amp; Metrology of SWNT Conductor Systems.</li><li>4. Electrodynamic Consolidation for Quantum Conductors.</li><li>5. Net-Shape Continuous Fiber/Cable Growth.</li><li>6. Fiber Bundle Re-Forming/Re-Crystallization.</li><li>7. Post-Processing Connectivity Optimization.</li><li>8. Microelectronic Interconnect Applications Research.</li><li>9. Aerospace Vehicle Signal &amp; Power Applications Research.</li><li>10. Motor/Generator Applications Research.</li><li>11. Quantum Wire Production and Scaling Plans.</li></ol>



# ARMCHAIR QUANTUM WIRE: DIRECTED RESEARCH & DEVELOPMENT

CARBON NANOTECHNOLOGY LABORATORY  
Rice University – Houston, Texas, USA

## Introduction

We propose a highly directed five-year program to develop scalable production, processing and manufacturing technologies for Armchair Quantum Wire (AQW). We envision AQW as a large quasi-crystalline assembly of specific Single Wall Carbon NanoTubes (SWNT) optimized for maximum electrical current carrying capacity. We fully expect that AQW will have at least the conductivity of copper at one-sixth its weight. Recent research results indicate that further order-of-magnitude improvements may be possible as well. The program has a firm foundation in the pioneering SWNT production, characterization and processing technology- and experience-base in Prof. Smalley's Group, the Carbon Nanotechnology Laboratory (CNL) team and collaborating institutions. Armchair Quantum Wire represents an important opportunity with potentially transformative impact across both Federal and Private sectors; a few are listed here:

Aerospace  
Electric Propulsion  
Power Distribution

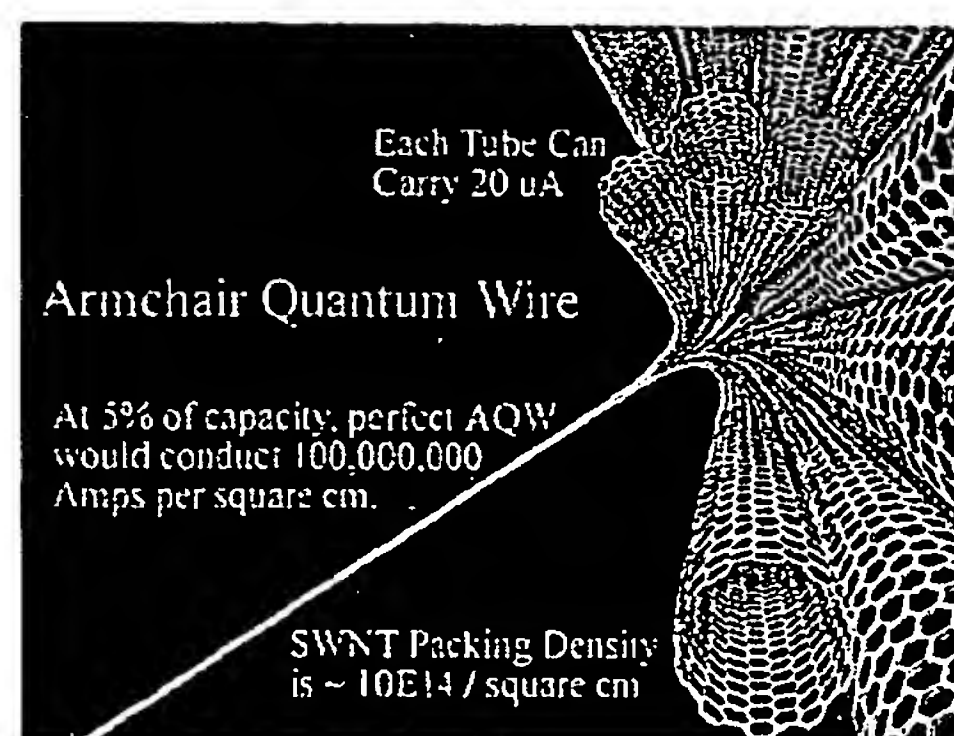
signal wiring, power harnesses and actuators  
primary drive motors, regenerative braking, servo systems  
high-power, long-distance power grids

Air Force, NASA, MDA  
Army, Navy, DOE/DOT  
DOE, FERC

Since SWNT are a pure carbon polymer with extremely attractive chemo-mechanical properties, AQW will enjoy a number of primary and multi-functional advantages compared to industrial alternatives, primarily copper and aluminum and their alloys. A representative list of material properties and potential impact follows:

Property	AQW / SWNT	Copper	Aluminum	Potential Impact
Electrical Conductivity	$10^4$ - $10^7$ mho	$5.3 \times 10^5$ mho	$3.8 \times 10^5$ mho	20-50% smaller, lighter motor/generators
Mass Density	1.4 g/cc	8.9 g/cc	2.7 g/cc	10-100 x lighter signal/power harnesses
Environmental	inert to 500C	corrodes	surface oxides	reduced maintenance, especially at sea
Thermal Expansion	-2 ppm $^{\circ}\text{C}^{-1}$	16 ppm $^{\circ}\text{C}^{-1}$	23 ppm $^{\circ}\text{C}^{-1}$	eliminate sagging cables in power grids
Thermal Conductivity	20-2000 $\text{Wm}^{-1}\text{K}^{-1}$	$< 400 \text{ Wm}^{-1}\text{K}^{-1}$	116-235 $\text{Wm}^{-1}\text{K}^{-1}$	thermal mgmt. multi-functional potential
Tensile Strength	5-20 GPa	0.4-1.5 GPa	0.1- 0.6 GPa	laminare multi-functional potential
Bulk Modulus	300-600 GPa	~30 GPa	~80 GPa	structural multi-functional potential

While our key objective, Armchair Quantum Wire, is both well-defined and clearly practical, we expect that the program will have positive, or even enabling, impact on many other SWNT application areas. These indirect benefits will arise from advances in key unit-processes, e.g. SWNT selection, cutting, cloning, production scaling, cleaning, processing and fabrication. Known SWNT application areas synergistically impacted will include fuel cells, ultra-capacitors, nano-electronics, structural composites, photovoltaics, sensors and bio/medical applications. Indeed, this effort will generate a transformative technology platform supporting many applications of this hyper-versatile engineering material, Single Wall Carbon NanoTubes.



The Armchair Quantum Wire concept is well grounded in oft-repeated observations of quantum, ballistic electron transport in individual metallic nanotubes at current densities above  $10^9$  amps per square centimeter – several orders of magnitude better than copper. This behavior is a direct and unique consequence of the nanometer-diameter, cylindrical structure and molecular perfection of the basic SWNT molecule. In essence, electrons can



only travel along the axis of the nanotube. For symmetry reasons, the typical electron scattering and energy loss mechanisms found in common metals simply do not exist in this material. Thus, properly selected SWNT can act like 'optical fibers for electrons', guiding high currents efficiently.

Practical AQW will consist of quasi-crystalline bundles of nanotubes of finite length. Calculations have shown that neighboring, aligned nanotubes will enjoy efficient tube-tube conduction through resonant quantum tunneling, as long as the tubes are of identical structure. This will largely bypass reflection effects at the ends of individual nanotubes – and provide a mechanism to preserve the quantum wires' microscopically outstanding conduction throughout the bulk of a macroscopic array of nanotubes. This does imply however, that we will have to fabricate AQW out of only one of the many types of available nanotubes.

Success in this venture will therefore also depend on developing a SWNT production process that delivers specifically structured SWNT. About one third of the possible SWNT structures exhibit metallic conduction. Of these we will focus on the "Armchair" family, depicted in the concept sketch above. Among SWNT, Armchair tubes have the highest density of allowed electron energy states, and have been predicted to be essentially impervious to defects, bends and similar imperfections that will inevitably occur in real-world macroscopic objects. Armchair tubes are also achiral and completely axially symmetric, ensuring that the conditions for resonant quantum tunneling are preserved in bulk articles.

Our approach for producing exclusively Armchair tubes efficiently and at low cost is called 'cloning'. In SWNT cloning, desired type(s) are selected from a now-typical SWNT mixture and propagated. Tubes are chemically cut into very small segments (20 nm) and "amplified" back to full production length (microns to tens of microns). We expect single-cycle gains on the order of one thousand or more in this system, as explained in detail below. This will enable bulk production of selected SWNT (Armchair tubes) starting from a very small quantity of material selected by chromatographic or similar means.

SWNT production processes to be perfected in this work will employ extremely low-cost feedstocks (e.g. CO/H<sub>2</sub> or methane) and moderate conditions (e.g. 600 °C at 500 psi). SWNT synthesis is catalyzed by inexpensive transition metals (e.g. iron, cobalt or molybdenum). Thus, the full-scale process and plant should be similar to those used for producing high molecular weight polyethylene, one of the cheapest industrial polymers. SWNT processing technology for making the final wire and cable products will most likely be based on fibers spun from concentrated sulfuric acid (oleum), another very inexpensive industrial chemical. This is the essentially the same technology used for spinning Kevlar and Zylon fibers affordably at the ton-scale.

At CNL, we think of Buckytubes as a new polymer of pure carbon, in the tradition of the great "miracle polymers" of the last century like Nylon, polypropylene and Kevlar. We expect that Buckytube production technology will follow a path similar to theirs. Initially, each of these polymers was produced in small amounts at low yield with many impurities. Today, these materials are produced in vast quantities around the world quite cheaply with extraordinarily efficient and elegantly specific catalysts. We believe that the new miracle polymer, Buckytubes, has a similar destiny. A key goal at CNL is to develop the processes that permit such rapid Buckytube development, and we believe the key break-through will come from prepared catalysts and growth from seeds. This approach will enable low-cost production of SWNT with total control over type, diameter and length under moderate conditions using cheap feedstocks like Syngas derived from coal.

The CNL Team at Rice is extremely well qualified and positioned to successfully execute this program. The Laboratory focuses the efforts of ten senior Rice faculty and their groups related to SWNT research and development. CNL was organized in 2003 as a unit of Rice's Center for Nanoscale Science and Technology (CNST). CNL team members are clearly leaders in carbon nanotube R&D, having developed three of the four known SWNT production methods, commercialized HiPco to the pound level, developed several robust SWNT functionalization chemistries, elucidated the basic signatures and spectroscopy of individual SWNT types, and developed superacid-based methodologies for spinning neat and composite SWNT fibers, among many other ground-breaking accomplishments. The program will be led by Professor Richard Smalley, Nobel Laureate and Director of the CNL. Co-Investigators will include additional CNL faculty from Rice University, faculty from collaborating universities, and researchers at Federal laboratories. We estimate financial support for the five-year program at \$25 million.



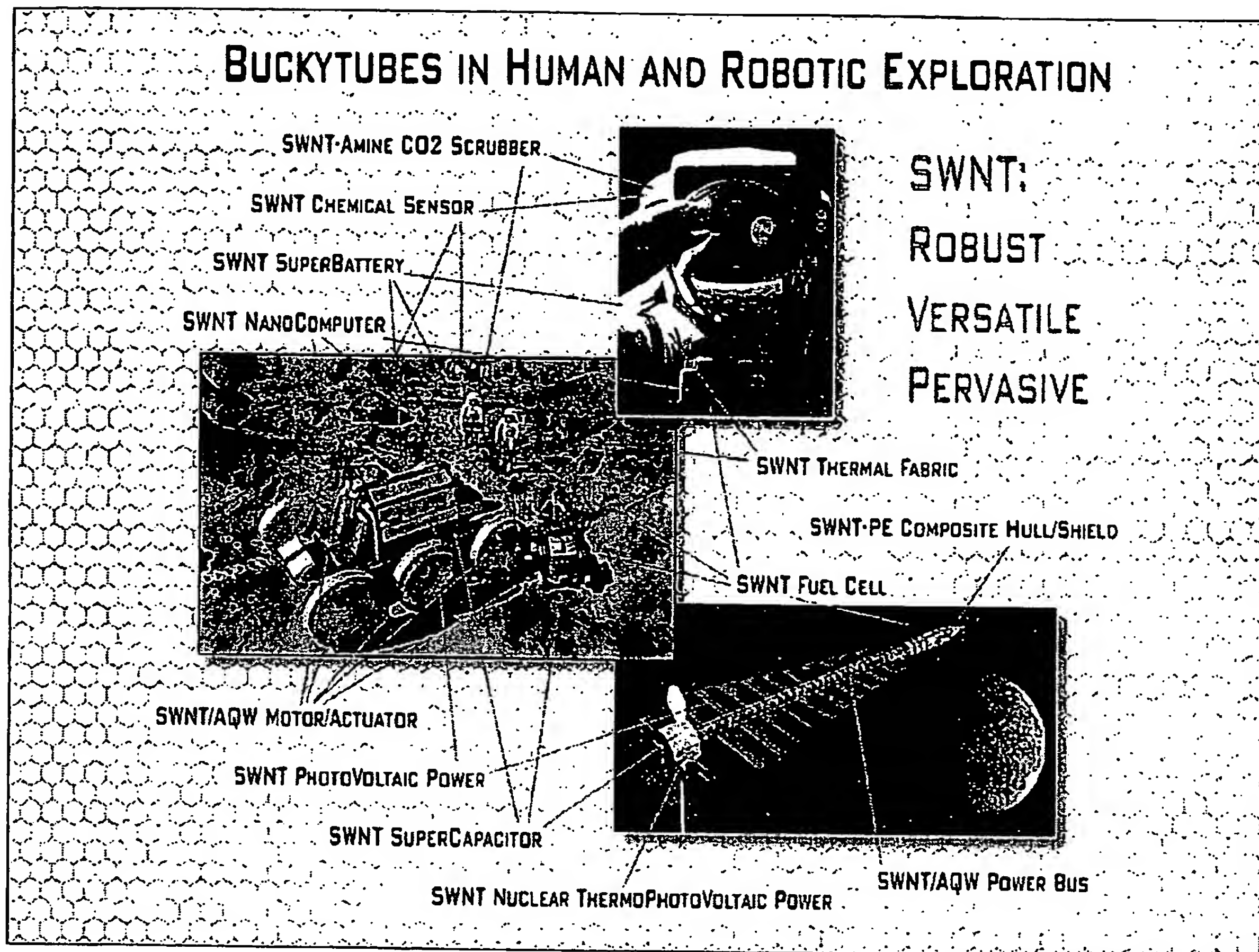
## Enabling Synergies

Success in the Quantum Wire program will have wide ranging benefits for Buckytube science, technology and applications well beyond the wire itself. The two broad enabling results of the program will be (n,m) control and substantial production cost reductions due to Cloning. We estimate that the cost target for type-selected SWNT for Quantum Wire should be about \$30 per kilogram – the cheapest application class in the table below. Most SWNT applications can be optimized by using a specific type or class of SWNT, like ESD composites and super-capacitors.

Indeed, some SWNT applications are simply impossible without exact (n,m) control and other technical capabilities to result from this program. For example, consider SWNT transistor arrays. This application requires supply of extremely pure SWNT of exclusively one (n,m) semiconducting tube – and these should be of a very well defined length. For processing, these will have to be solubilized through sidewall functionalization chemistries. For arrays assembly, these will also need different and specific chemical functionalizations on each end. All such functionalizations will also have to be very cleanly removable to yield pristine buckytubes with well defined electronic and optical properties. Finally, low resistance contacts, as needed for AQW will be needed to connect these nanotube elements into circuits.

We have a high degree of confidence that SWNT Armchair Quantum Wire could revolutionize the world of electrical power and signal transport. Even if it does not meet our full expectations, however, the technology developed during this program will enable many other valuable applications and capabilities, and firmly establish Buckytubes as routine engineering materials. The following table shows a non-exhaustive list of potential SWNT applications and estimated cost, type, functionalization requirements.

SWNT Requirements	SWNT cost \$ / kilo	(n,m) control	(l) control	purity # nines	Additional requirements
<b>SWNT Applications</b>					
Bio-Probes/Therapies	30,000	yes	precise	6	extreme purity, end func.
Chemical Sensors	10,000	yes	some	6	mult. types, full func., directed assy.
Molecular Electronics	3,000	yes	precise	6	semis, full func, directed assy.
Photovoltaics	3,000	yes	some	6	semis, end func.
Electronic Interconnect	1,000	yes	some	5	metals
Photocatalysts	1,000	yes	some	4	
Heat Pipes	1,000	yes	no	2	long SWNT, cont. growth, non-metals
Aero signal/power buss	100	yes	no	3	
Heat Sinks/Spreaders	100	no	no	3	long SWNT, membranes, non-metals
Advanced Batteries	30	yes	no	2	metals, controlled dia./spacing
Supercapacitors	30	yes	no	3	metals, controlled dia./spacing
Hydrogen Storage	30	yes	no	3	controlled dia./spacing
High Performance Fibers	30	no	yes	3	
Power Grid Cable	30	yes	no	3	
3D Structural Composites	30	no	no	3	
ESD Composites	30	no	no	2	

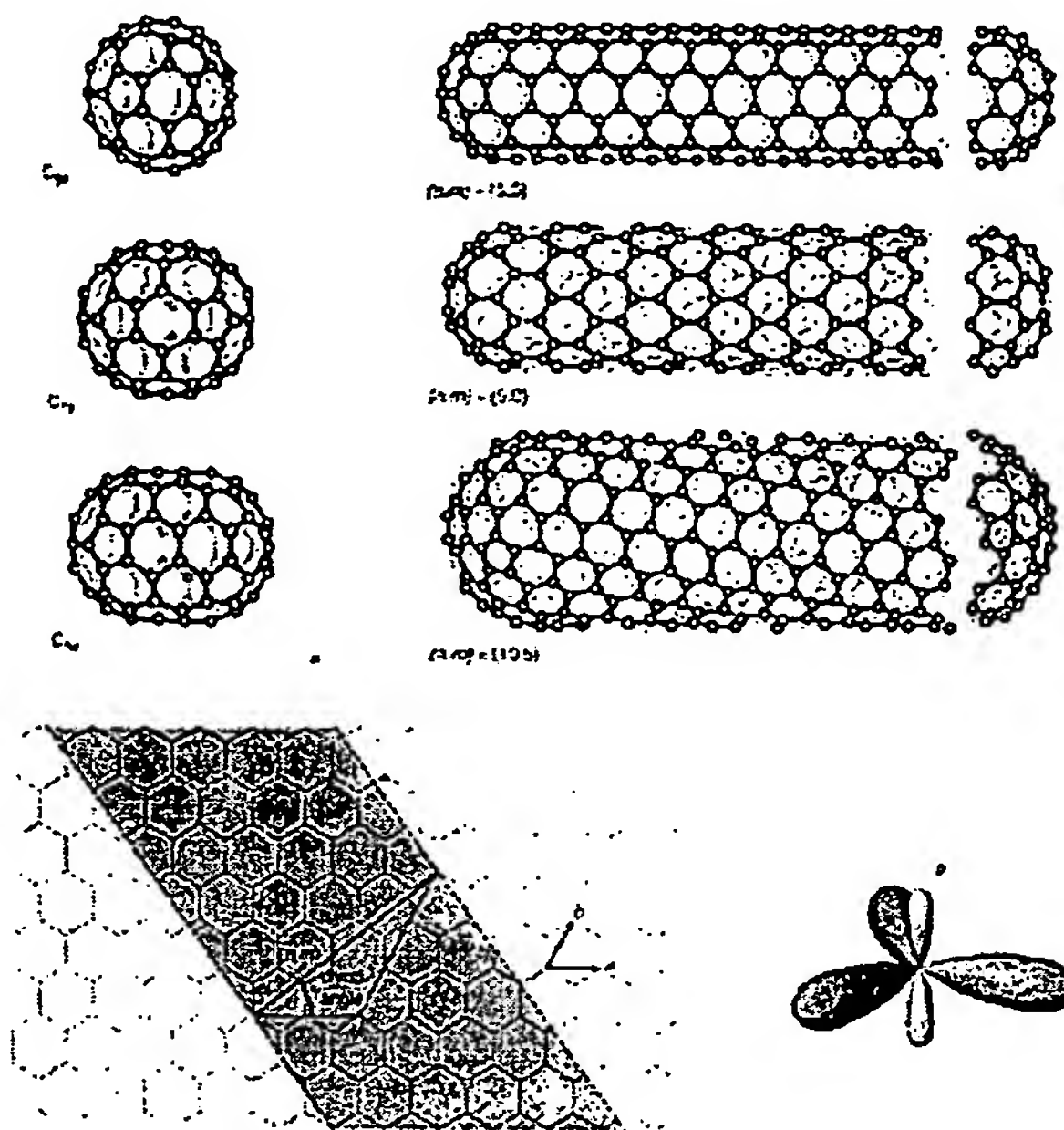


Potential SWNT Applications Span Many Human and Robotic Exploration Capabilities.

## Technical Background & Approach

Single Wall Carbon Nanotubes (SWNT). SWNT comprise a class of potentially ideal nano-engineering materials for a wide range of disciplines. While SWNT research and development is aggressive world-wide, and accelerating rapidly, key barriers to full-scale exploitation remain - primarily cost, purity and processing. The economic impact and defense capabilities enabled by resolving these issues successfully are significant. These factors combine to make a compelling case for establishing an intense research and development program encompassing production, processing and manipulation of selected SWNT types, the subject of this proposal.

SWNT [1] are family of cylindrical pure-carbon polymers roughly one nanometer in diameter; individual molecules can range in length from a few nanometers to over one centimeter. One can envision these 'Buckytubes' as being rolled-up from a slice of 'graphene' sheet, with Buckyball halves at the ends. The basic graphene strip can be 'cut' at various angles and of various sizes - resulting in designs for the roughly 100 observed types of Single Wall Carbon Nanotubes. SWNT in general are the strongest and toughest material possible; SWNT also display extremely high thermal conductivity along their axis. Depending on their exact bonding pattern, individual SWNT molecules display a variety of electronic configurations: metallic, semiconductor, or semi-metal. Metallic tubes are among the best conductors known; the semi-conductors have direct band-gaps and extremely high carrier mobility [10]. Insulating tubes can also be produced by organic chemical modifications. SWNT also have the highest possible surface area of any material, since every atom is accessible on the outer tube surface as well as the interior pore.



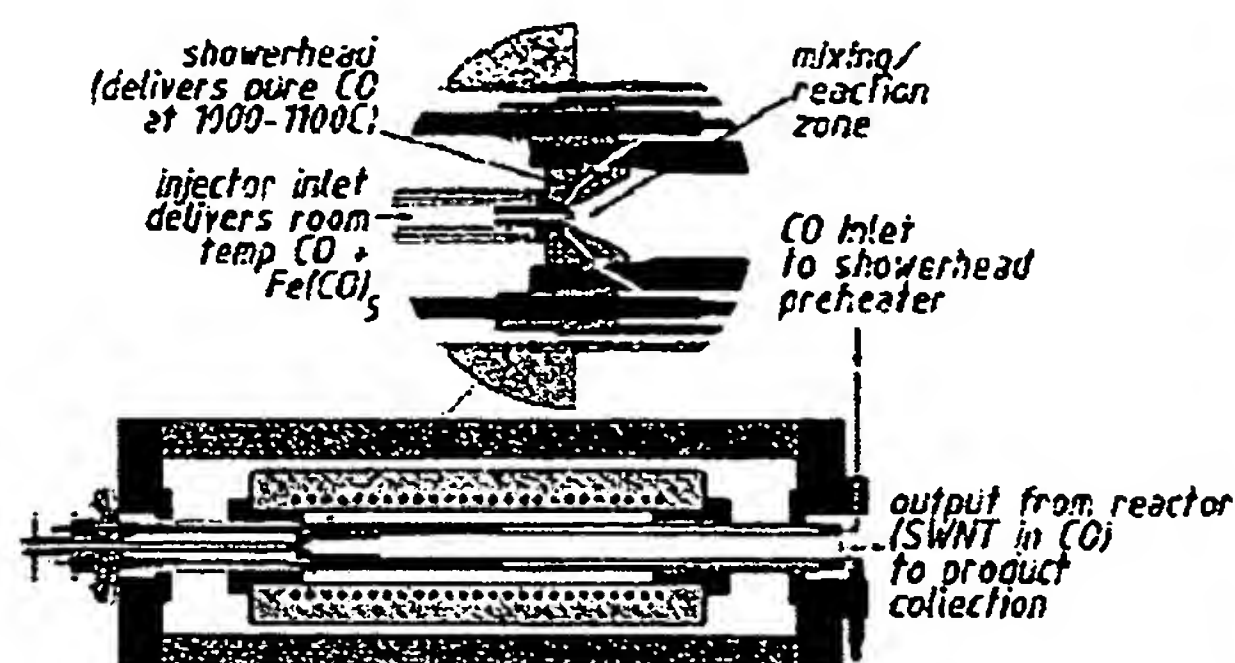
Many applications exploiting their extreme physical properties [2,5,6,7] (strength, toughness, conductivity, carrier mobility, surface area, etc.) have been demonstrated or are under development. Macro-scale applications include high performance composites, conductive polymers, morphing structures and electrodes for fuel cells and supercapacitors; nano-scale applications include sensors, emitters, interconnect and transistors. SNWT surely represent the ultimate in multi-functional materials: one basic material system provides metals, insulators and semiconductors as well as elements bridging nanometer to macro-scale systems.

SWNT production has progressed a long way since their fortuitous discovery in arc soot in 1991 [3,4]. The leading process for making SWNT, called HiPco (High Pressure CO), was developed at Rice in Prof. Smalley's laboratory. The process has been transitioned to commercial operation, with production rates between and 20 and 50 pounds a day expected in mid-2004. Nanotubes grow from nanometer-diameter transition metal catalyst particles (typically Iron), which are generated *in-situ*, e.g. by pyrolysis of iron pentacarbonyl. Carbon is continuously supplied in the form of CO at high pressure; at reaction temperatures (about 950 C), CO dissociates on the catalyst surface to C and CO<sub>2</sub>. As carbon accumulates on the catalyst particles, it forms partial fullerene shells; some of these detach from the metal and serve as the nucleation site for Buckytube growth. Under the influence of the catalyst particle, the free carbon is essentially polymerized onto the growing nanotube, which grows at locally phenomenal rates: around 1 mm per second. Nucleation is rather inefficient and certainly inexact, but the fast growth rate ensures that the bulk of the product is indeed Single-Wall Carbon Nanotubes of high molecular perfection.

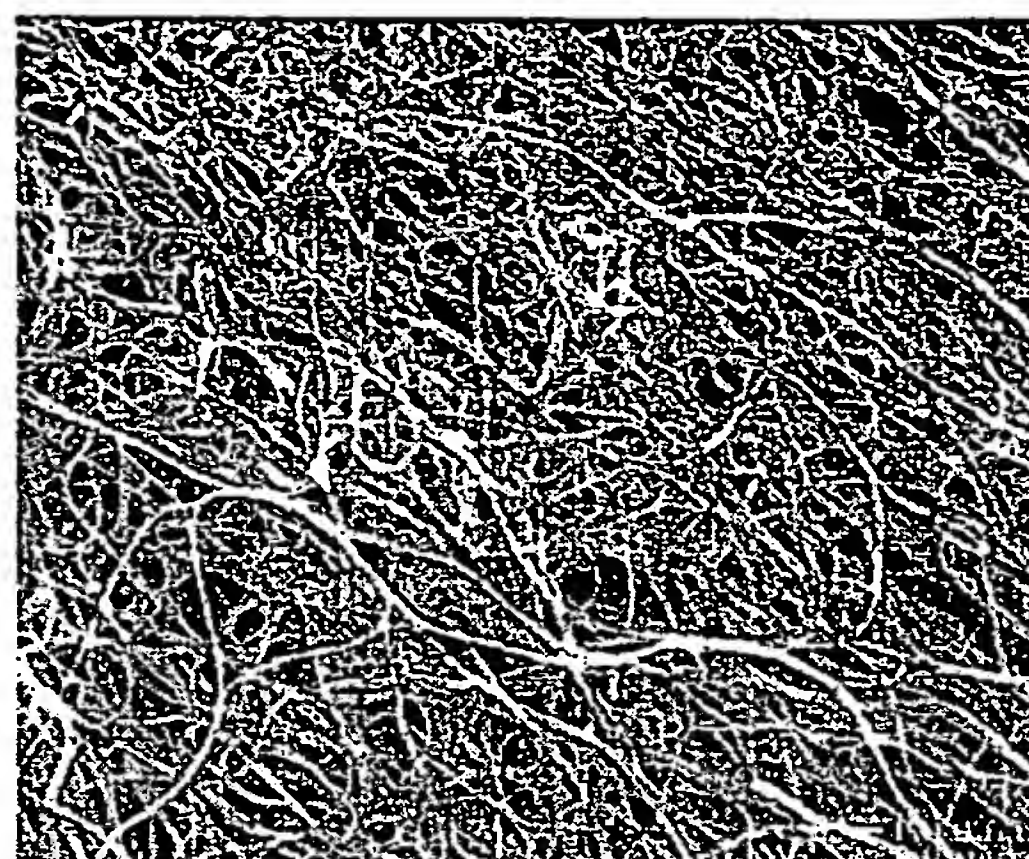
Raw SWNT material (from all sources) therefore contains not only a mixture of SWNT types (n,m) bundled into primordial 'ropes', but also left-over metal catalyst, fullerene shells of many sizes, and metal particles over-coated with relatively thick layers of graphite. These by-products have to be removed by laborious purification steps



before the SWNT material can be used for most applications. The process and its nominal product are shown in the following figure.

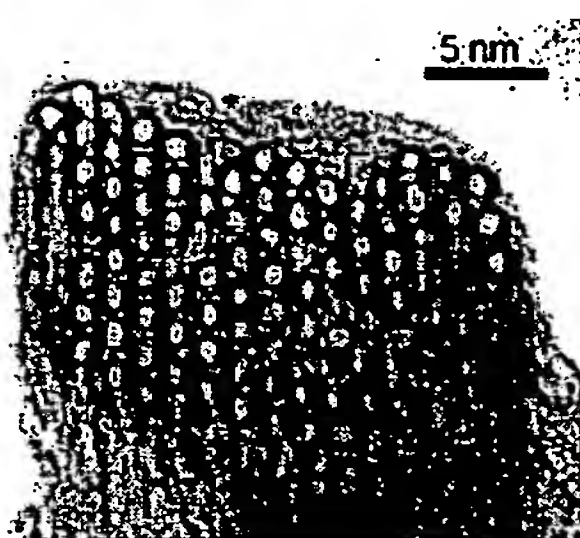


HiPco Is The Standard SWNT Production Technology Today

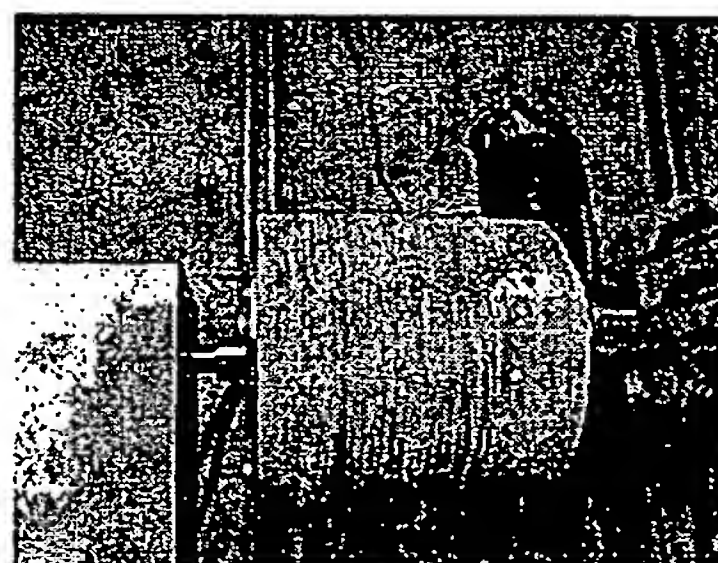


Raw HiPco Product Is A Mat Of SWNT Ropes

**Processing & Spinning.** CNL has pioneered cleaning and post-processing technologies for fabricating both nano-derivatives and macro-scale articles out of SWNT building blocks. This is not without its challenges. SWNT are extremely polarizable and display very strong Van der Waals attraction for one another – hence their famous tendency to aggregate into quasi-crystalline ‘ropes’. The VDW energy is roughly 0.5 eV per nanometer of a pair of tubes in contact. Under cavitation conditions SWNT can be completely separated by surfactants at low yield [8]. We have demonstrated that super-acids, e.g. oleum, can effectively intercalate and ‘lubricate’ ropes, allowing for processing into films and fibers [9]. This provides a key starting point for forming wires and cables from future, optimized SWNT materials. Figures illustrating ropes and oleum-spun neat SWNT fibers follow:



Hexagonal SWNT Self-Assembly

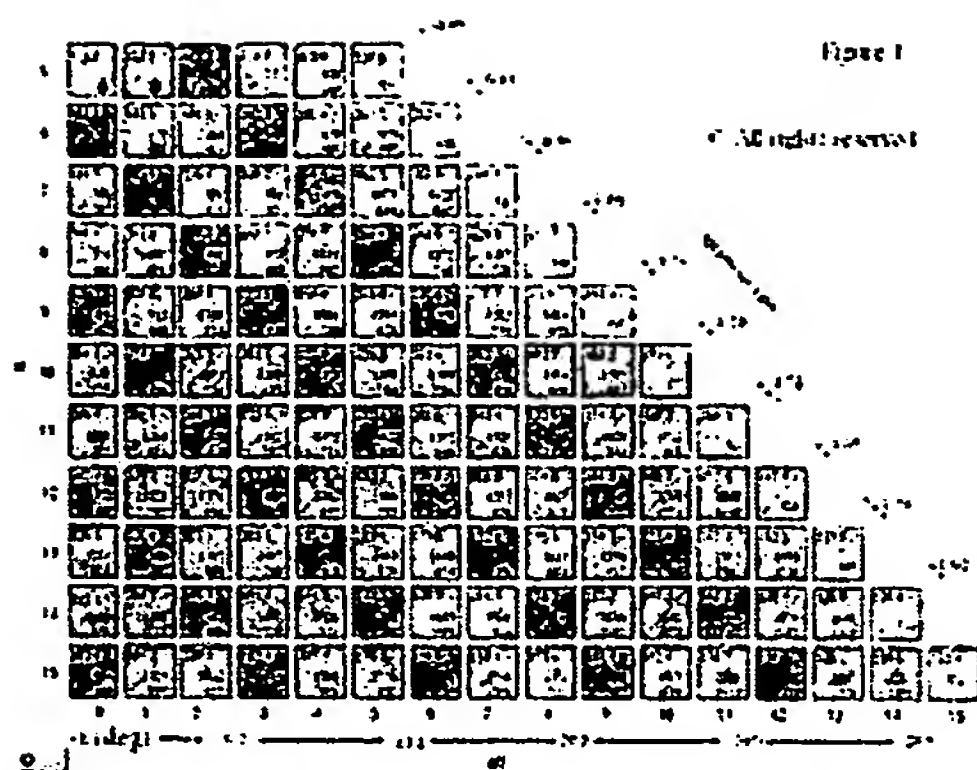


SWNT Fibers Spun From Oleum

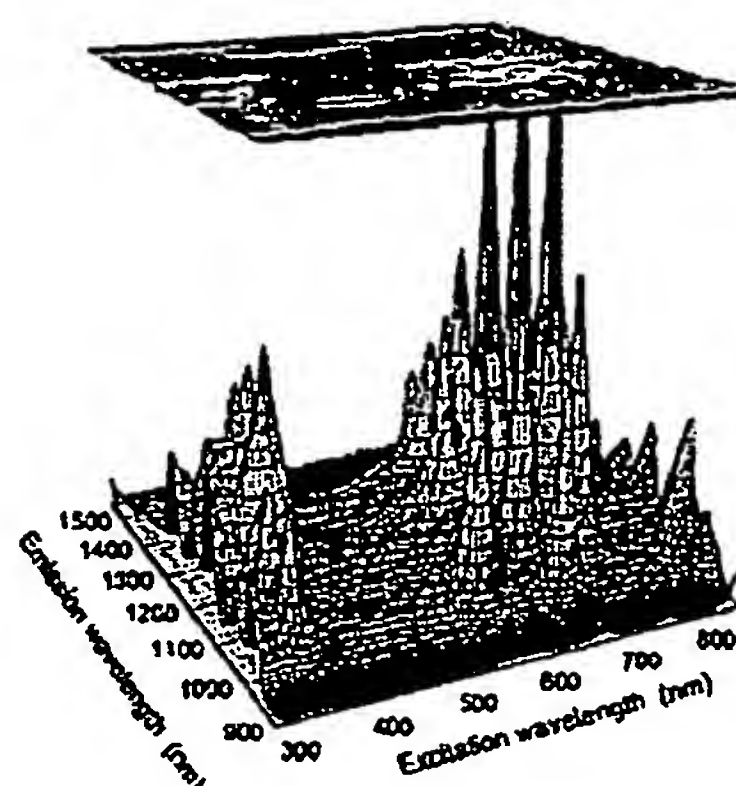


SWNT Fiber & “Super-Rope” Detail

**SWNT Type (n,m) Complexity.** We stated above without detail that SWNT come in many different ‘roll-up’ configurations – in fact, there are some 58 observed types to date. Each (n,m) configuration has a very specific spectroscopic signature, and demonstrates the number of electronically distinct SWNT types [18]. The following Figures show a ‘Periodic Table of SWNT’ developed by CNL staff, as well as an excitation-fluorescence spectrum from a mixture of SWNT; each peak in the spectrum corresponds to one unique type of nanotube.

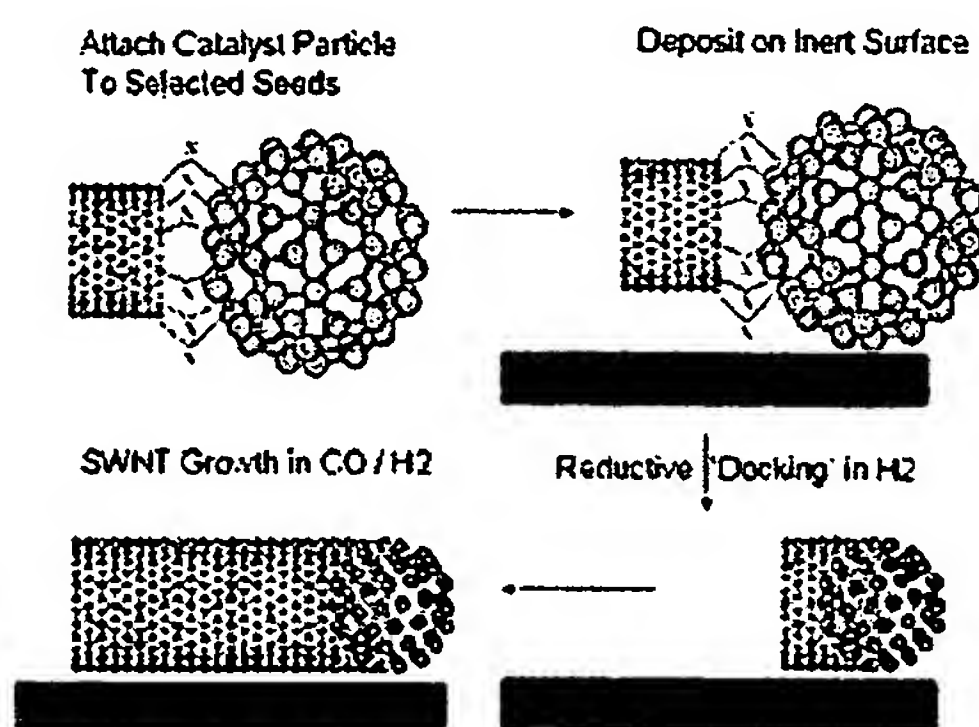


In This (n,m) SNWT Table, Blue = Truly Metallic (Armchair),  
Green = Semiconductors (Chiral), Yellow = Semi-Metals.

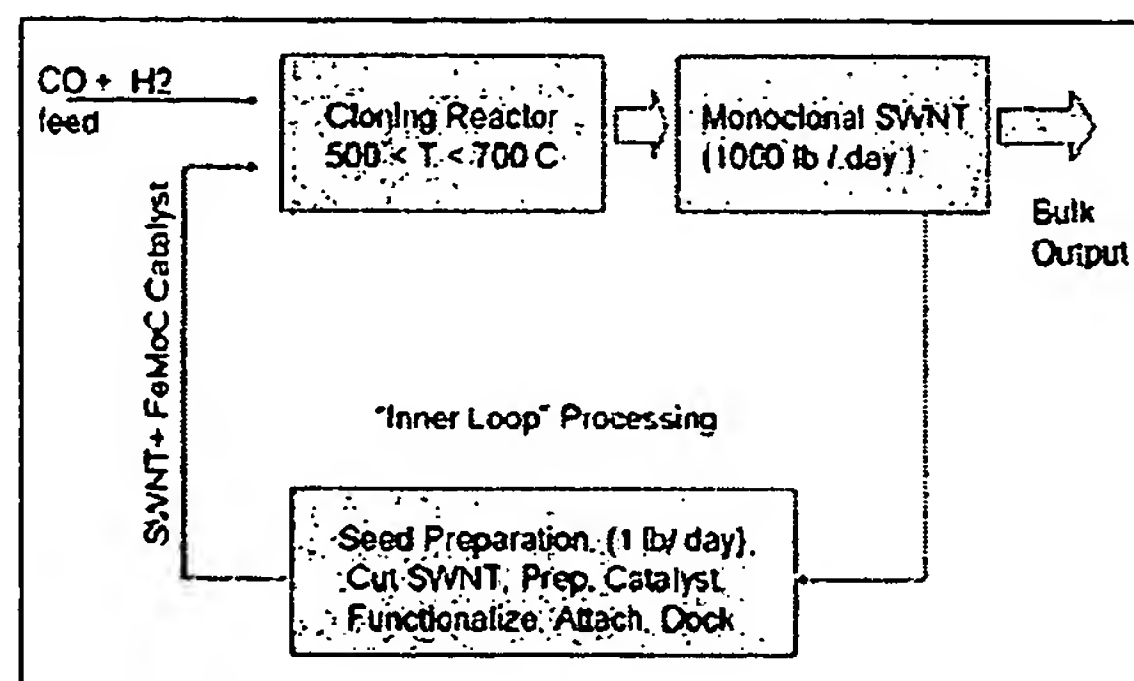


Each Peak Is Unique To A Particular SWNT Type

**Cloning.** A key CNL innovation that will enable type-specific, low-cost production is 'Cloning'. By separating and completely controlling the nucleation and growth cycles, we expect that this technology will eventually enable ton-level production at roughly \$30 per pound. The key conceptual break-through in cloning is, for the first time ever, totally separating the nucleation and the growth of carbon nanotubes. As described above, nucleation is random, resulting in several by-product channels and degrading yield. Moreover, and as we shall see, more importantly for the AQW program, a mixture of SWNT types are produced from spontaneous nucleation and growth in the same chamber. Fortunately, we have demonstrated that nucleation from the vapor phase only occurs at temperatures over 900°C, whereas the fundamental growth process can proceed at temperatures as low as 500°C. To run at lower temperatures, we have to deliberately provide both pre-formed catalysts as well as 'starter tube' templates for growth. The cloning concept and reactor/process schematic appear in the following figure.



SWNT Seed Preparation Scheme



BuckyTube Cloning Production Scheme

Since production from clonal seeds will proceed at moderate temperatures and with high purity, we expect that the cost and complexity of the reactor will be minimized, and the throughput and cost of SWNT production will improve dramatically. Two key unit processes that enable success in cloning are a) cutting SWNT to short regular lengths, and b) viable catalyst production and attachment pathways.

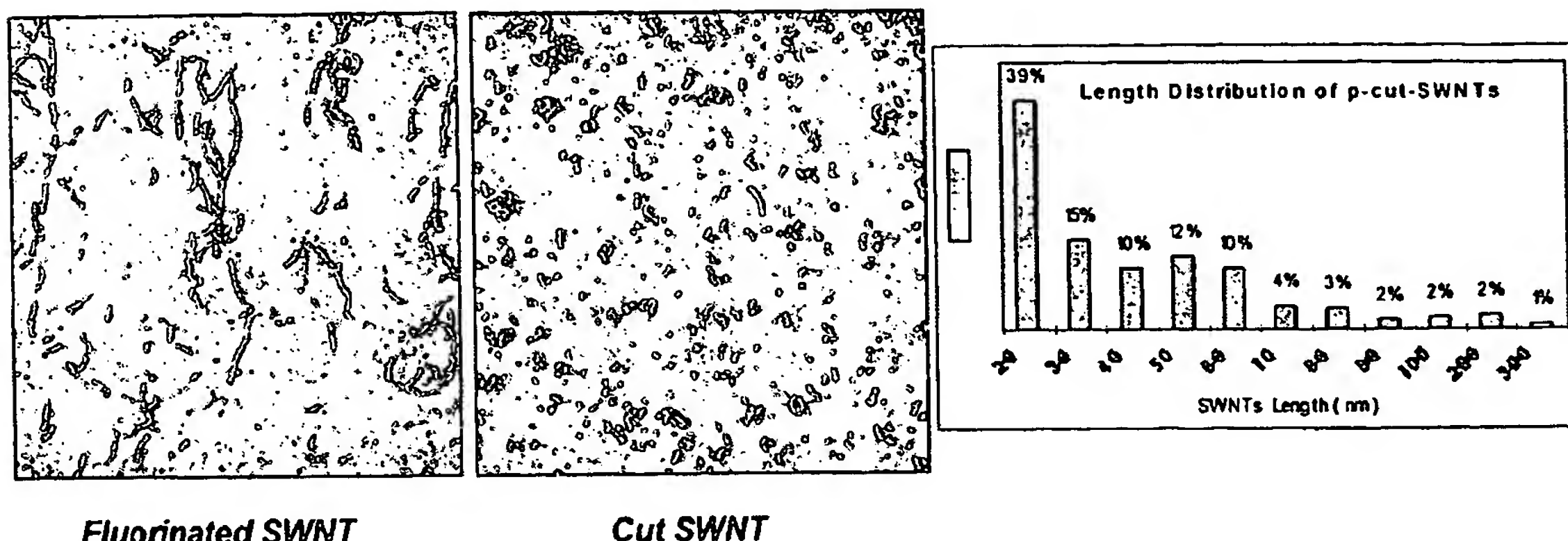
**SWNT Cutting.** Efficient SWNT cutting processes are particularly needed to achieve 'gain' in a cloning reactor. Cutting processes are also needed for a number of SWNT applications, e.g. nanoelectronics and block-copolymer composites. While the SWNT structure is normally almost impregnable, it is susceptible cutting and defect formation under certain extreme conditions. For instance, we have encouraging initial results on cutting via aggregates of chemisorbed electronegative atoms, especially fluorine and oxygen. These are delivered as di-fluorine [11] and ozone, respectively. While the mechanism is not clearly understood, it appears that initial adatoms 'direct' additional chemisorption at adjacent sites, resulting in clusters of fluorine or oxygen. Upon thermolysis, these clusters, or bands



fluorinated SWNT

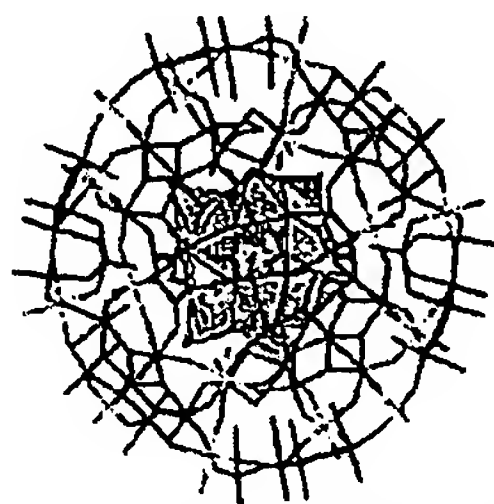


(shown in the adjacent figure), react with the nanotube generating  $\text{CF}_2$  and  $\text{CF}_4$  or  $\text{CO}$  and  $\text{CO}_2$ , respectively. Preliminary AFM results of cutting SWNT with fluorine are shown below, along with size statistics:

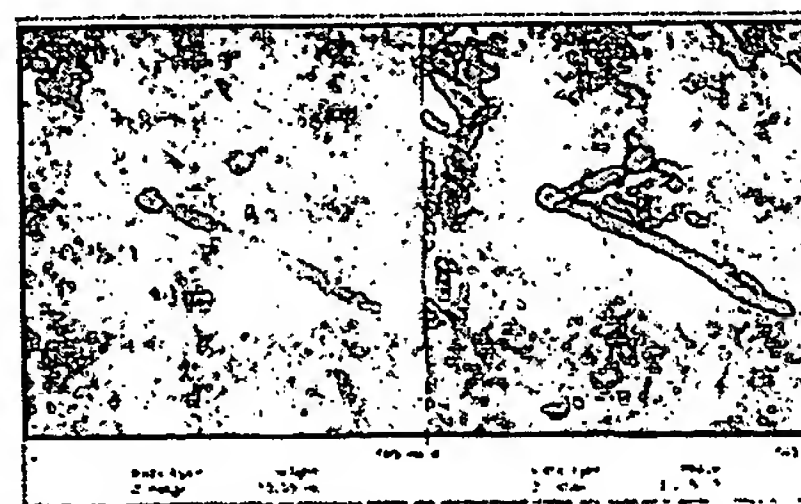


This two-step defect-cut process can be conceptually generalized. Thus, we have begun to explore radiolytic means (e.g. energetic electrons, photons and ions) means to produce the initial defects, with a particular focus on 3 MeV electron beam processing. This is a routine and relatively inexpensive industrial process. While it is known that electrons with kinetic energy over 87 KeV can directly remove carbon atoms from SWNT, the cross section is rather low. We hope to increase defect efficiency via 'chemical amplification' by irradiating in an environment that can produce energetic halogen (e.g. F, Cl) or chalcogenide (e.g. O, S) atoms adjacent to the SWNT. This takes advantage of the fact that extensive ionization and excitation occur along the electron track. The chemically active environment is achieved by intercalating SWNT ropes prior to irradiation (e.g.  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{SO}_4$ , etc.) Radiolytic excited oxygen should attack SWNT sidewalls readily, as this is a known process in low-pressure plasma systems. We will then exploit these defects by thermolysis and/or chemical oxidation, as with Pirana etch, to complete the cutting process.

**Catalyst Attachment.** The second critical 'inner loop' step is catalyst synthesis and attachment. We have a veritable arsenal of viable approaches for rational process design here, based upon known surfactant-mediated metal nanoparticle condensations, coupled with verified SWNT end functionalization chemistries [15] to bring the cut tubes and catalyst particles into contact with each other. However, we have fortuitously discovered what is likely an optimal path based on self-assembled Keplerate clusters, and natural coordination chemistry linking these to oxidatively cut nanotubes. Keplerates are self-assembling quasi-spherical clusters of mixed metal oxides. Among this large family of compounds is one that we lovingly call 'FeMoC' (Fe for Iron, Mo for Molybdenum and C for Cluster), shown schematically below [12]. FeMoC is comprised of an outer icosahedral shell containing both Mo and Fe ( $\text{H}_4\text{Mo}_72\text{Fe}_{30}(\text{CH}_3\text{COO})_{15}\text{O}_{254}(\text{H}_2\text{O})_{98}$ ) and an inner Mo cluster ( $\text{H}_x\text{PMo}_{12}\text{O}_{40}$ ). All told, the cluster contains 114 transition metal atoms and it is 2.1 nm in diameter in its native oxidized state. The cluster has already been demonstrated to reduce to an effective nanotube production catalyst under SWNT growth conditions [13, 14]. This is a chemically perfect and consistent reagent for SWNT catalytic growth. The material is not expensive, and we can already produce FeMoC in gram quantities with high yield. Fortune smiles further in that FeMoC is readily soluble in common solvents like ethanol, and its sphere of coordinated water molecules can be readily displaced by the poly-carboxylate groups native to the ends of oxidatively cut SWNT. We are currently working on a demonstration of the cloning process; the figure below shows an AFM of self-assembled nanotubes-FeMoC units sitting on an HOPG surface.



FeMoC: An Ideal And Affordable Cloning Catalyst



Cut-SWNT and FeMoC Self-Assemble In Solution (AFM Image)

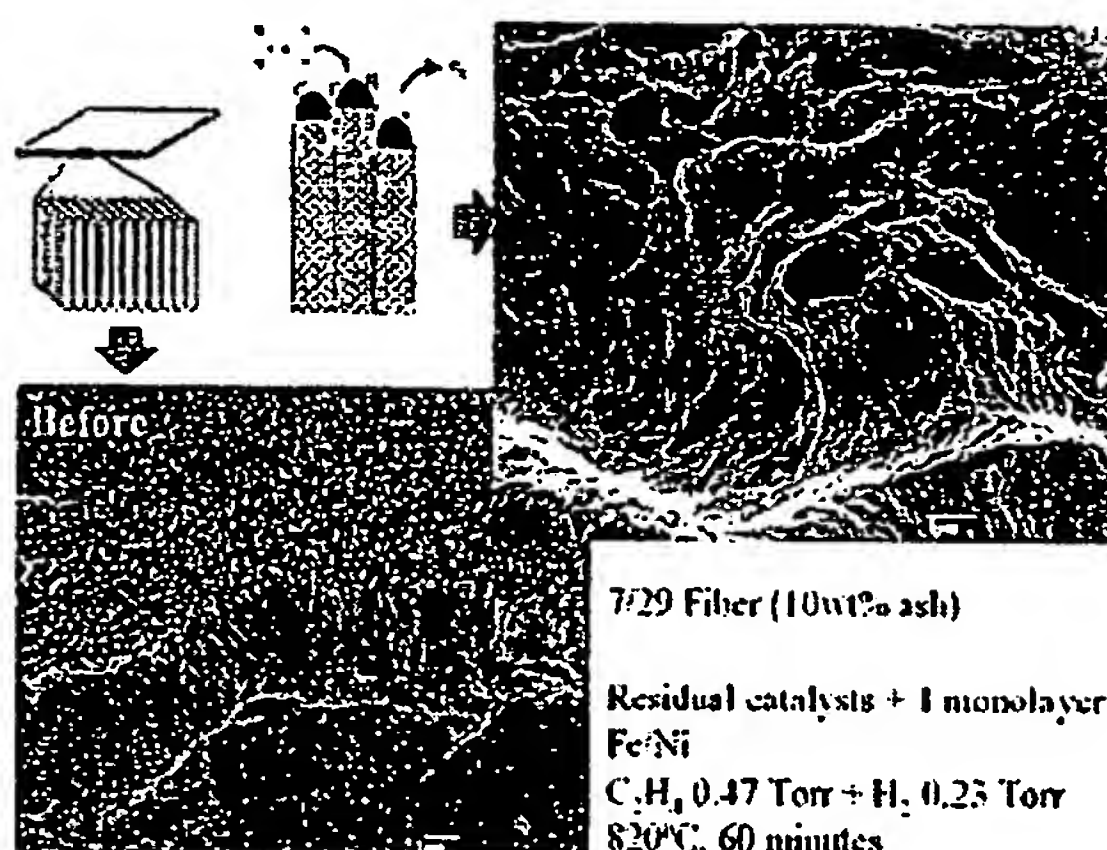


After we choose a particular cutting/catalyst/growth process, we will go about developing a new generation of optimized Cloning Reactors. There are two fairly obvious approaches a) HiPco-like using injected seeds, and b) supported growth based on seeds sitting on sacrificial high-surface area refractory powders. The latter could be based upon either fixed- or fluidized-bed designs; both are well-known industrial technologies.

**Continued Growth & Membranes.** An additional approach to be explored would grow conductive fibers in near net-shape as a film or aligned membrane. This is similar to what we call 'continued growth'. We have in-hand some results indicating that this is indeed possible. The SEM images (figure, right) show partial continued growth from a neat SWNT fiber. The material was composed of mixed HiPco SWNT. The re-nucleation efficiency is currently rather low with evaporated thin metallic catalyst films, but these results demonstrate conceptual feasibility of continued growth.

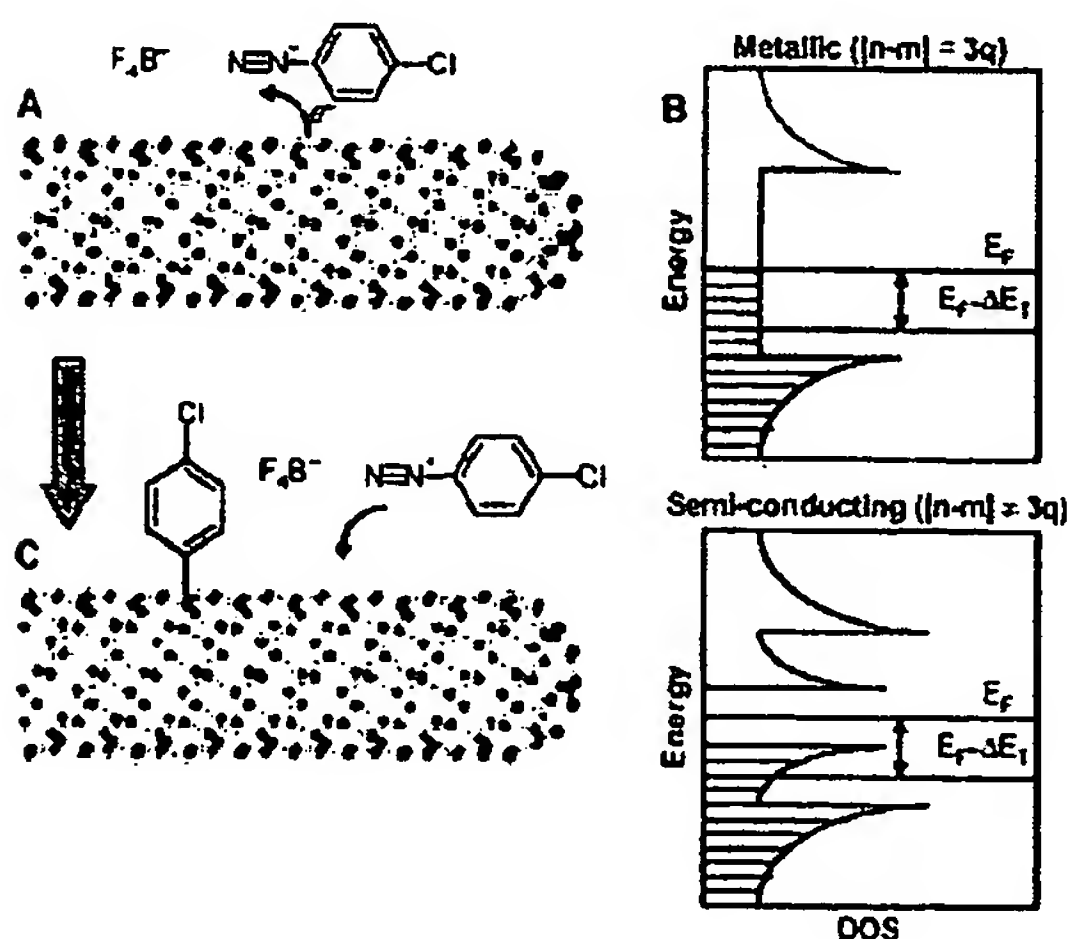
CNL researchers have also recently produced self-assembled monolayers (SAM) of FeMoC on various substrates, as well as progress towards SAMs of SWNT with attached nanotubes. Such assemblies will be explored as starting materials for clonally pure aligned SWNT membranes and structures.

The Continued Growth from a "Bed-of-Nails" like substrate

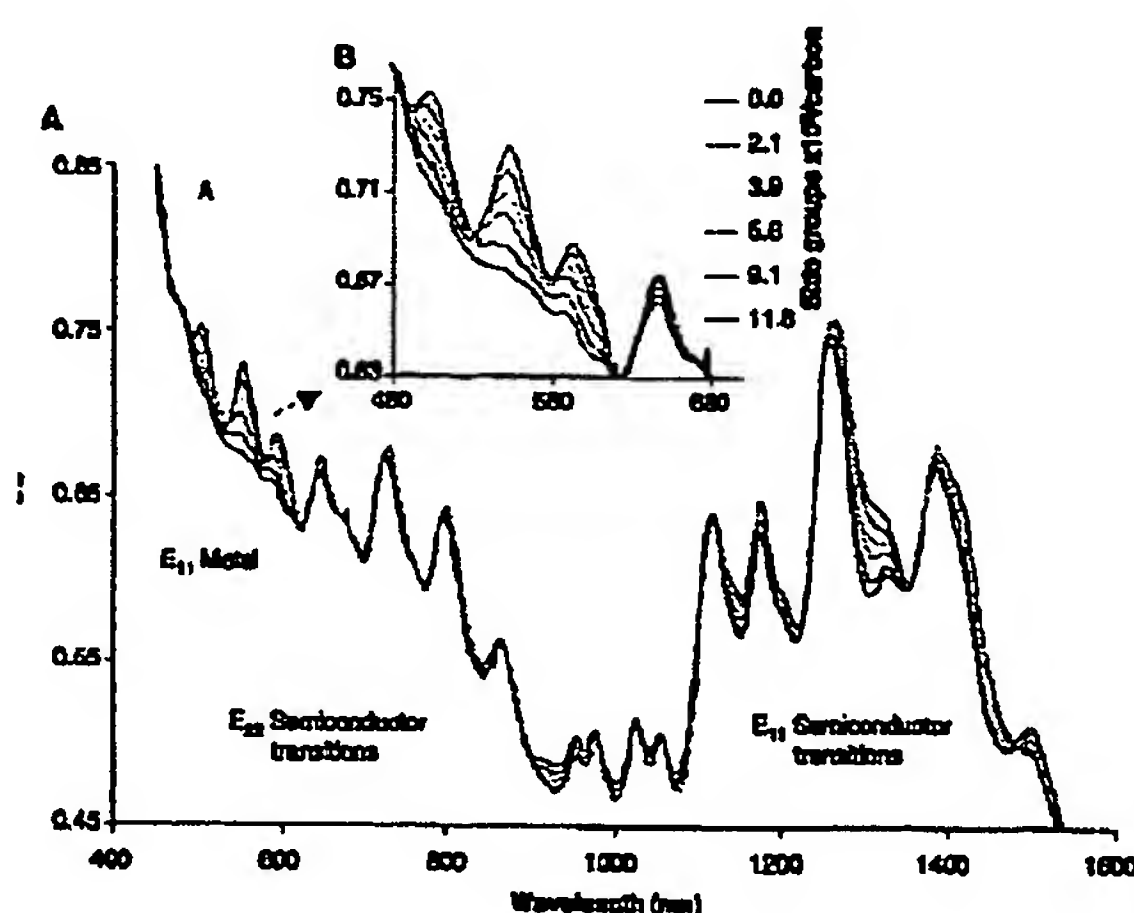


Partial Continued Growth of Neat SWNT Fibers

**SWNT Type (n,m) Sorting.** We will initially require milligram quantities of selected metallic tubes as feedstocks for cloning production. After experimentally surveying the bulk conductive characteristics of several chosen candidates, we expect to concentrate SWNT and AQW production efforts on the single best type. Using mixed feedstocks from existing HiPco production, we plan to extract selected SWNT by a combination of chromatographic techniques [31] and selective chemistries, both proven [15] and novel. For instance, we have recently demonstrated that metallic SWNT can be preferentially side-wall functionalized with selective free-radical adducts [15] (figure below, left). This process enables simple and efficient separation of metallic from semiconducting tubes in a surfactant-stabilized aqueous solution. The figure below, right shows the progressive functionalization of metallic tubes, as observed by UV-Visible absorption spectroscopy.



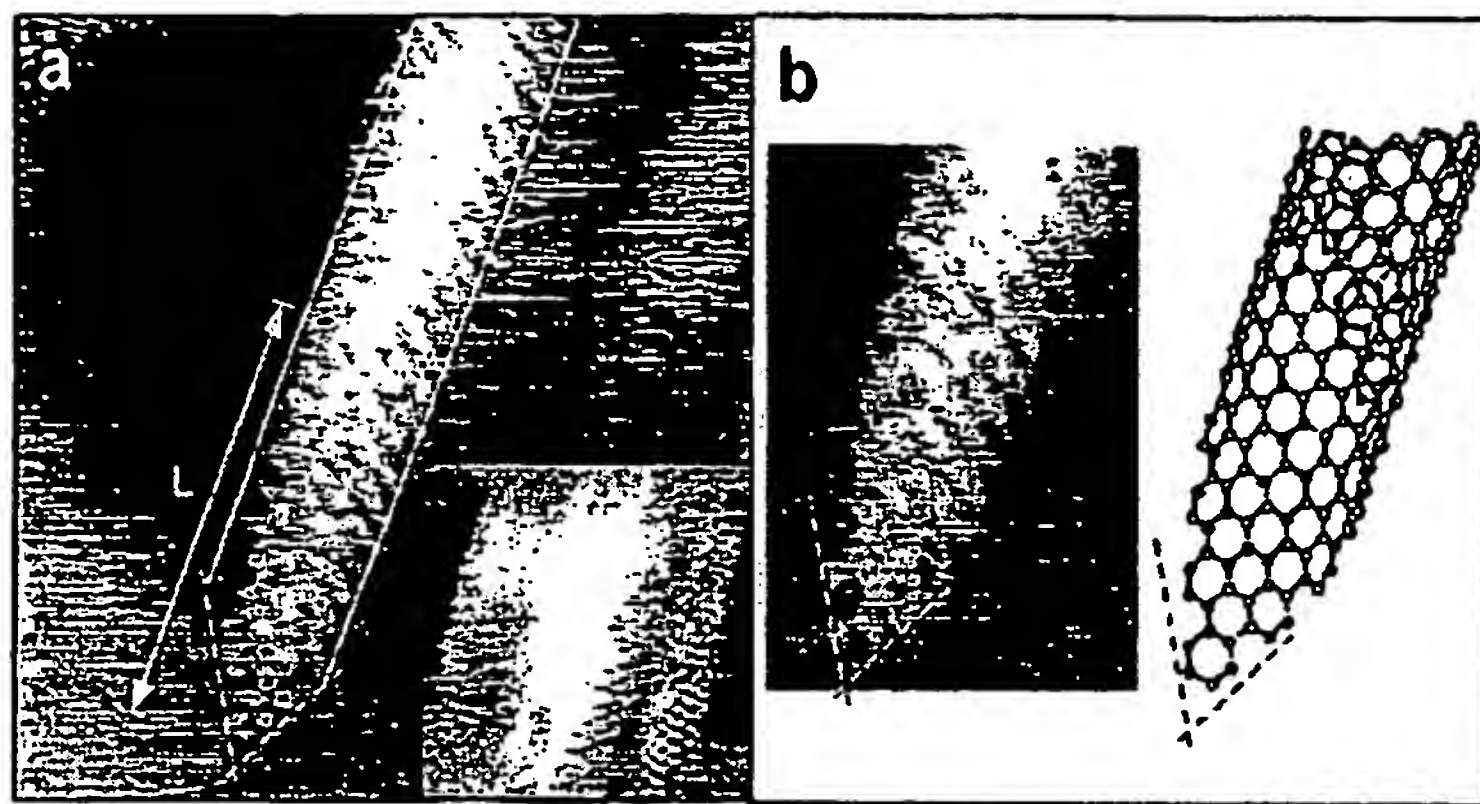
Selective Functionalization Separates SWNT By Class. [15]



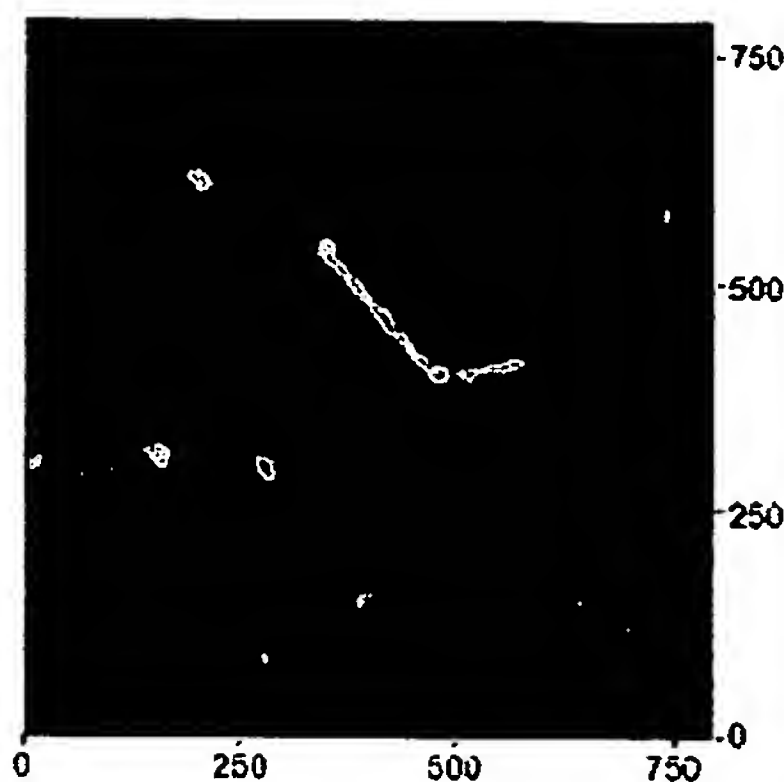
Type-Selection Can Be Monitored In Real-Time. [15]

More specific separations will be based upon the unique end-chemistry of oxidatively etched nanotubes. As Lieber [20] recently observed, chemical oxidation of SWNT preferentially exposes all-armchair edges at the ends of the tubes (see figure below, left). We know from our earlier work on "fullerene pipes" [32], that the ends of

etched SWNT are decorated with carboxylic acid groups. Indeed, these form the basis for end-functionalization chemistries that support attachment to metal particles. In the 'seven minutes to three' AFM image (below, right), shortened nanotubes were attached to gold particles using thiol terminated alkyl chains attached to SWNT via such carboxylic groups.



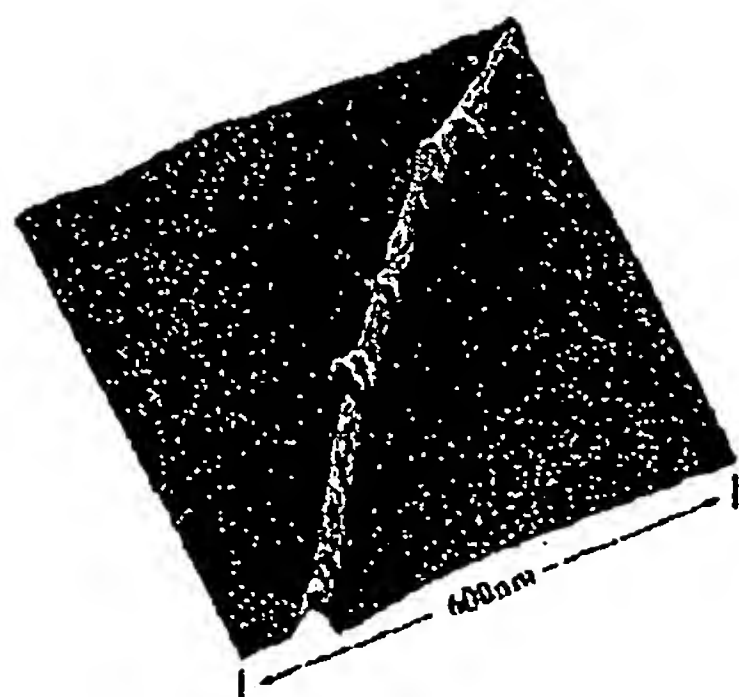
Distinct (n,m) values lead to unique end chemistries and geometries. [20]



End chemistries attach metal particles. [32]

As such, distinct SWNT (n,m) types have unique chemical signatures determined by their chirality and diameter – both in terms of the number of carboxylic acid groups, as well as their spatial extent and geometric arrangement. For instance, the minimum number of acids would be expected on small diameter 'armchair' tubes – the kind we plan to use for building quantum wire and cable. Earlier work [31] defined a general approach to separating tubes based on differential drag in capillary electrophoresis of surfactant-suspended SWNT, even though complete separation was confounded at the time by a multiplicity of lengths and charge-masking effects of the surfactants. Recent CNL advances in SWNT sidewall functionalization by a number of routes now generate individualized SWNT completely soluble in both organic and aqueous media. By combining these methods, and simplifying their implementation using short segments of cut tubes (see above), we expect to be able to obtain pure samples of selected SWNT for amplification and AQW production.

A pair of highly specific and novel separation methods, based on antibody affinity and photo-ablation, will also be explored. It has been already demonstrated that fullerene-specific antibodies [33] can be produced and attached to SWNT [34], as shown in the AFM image below, left. It is reasonable therefore that we should be able to develop specific antibodies for the etched ends of each (n,m) type of SWNT and use tethered versions of these for total separation in affinity chromatography columns. The second approach will exploit the meta-stable nature of surfactant-suspended SWNT micelles [15] (figure below, right). Here we will utilize photo absorption features specific to particular (n,m) and SWNT classes to de-solvate and precipitate SWNT from suspended mixtures. For example a tunable pulsed IR laser would be used to dynamically and selectively heat SWNT with a particular IR feature (radial breathing mode absorption); these would then flocculate from the aqueous suspension. Similarly one could use a pulsed broadband far-infrared source to selectively unwrap and precipitate metallic tubes. Centrifugation (used to form the original surfactant 'decants') would then be used to separate SWNT populations of interest.



Fullerene-specific antibodies (bumps) bind to SWNT. [34]

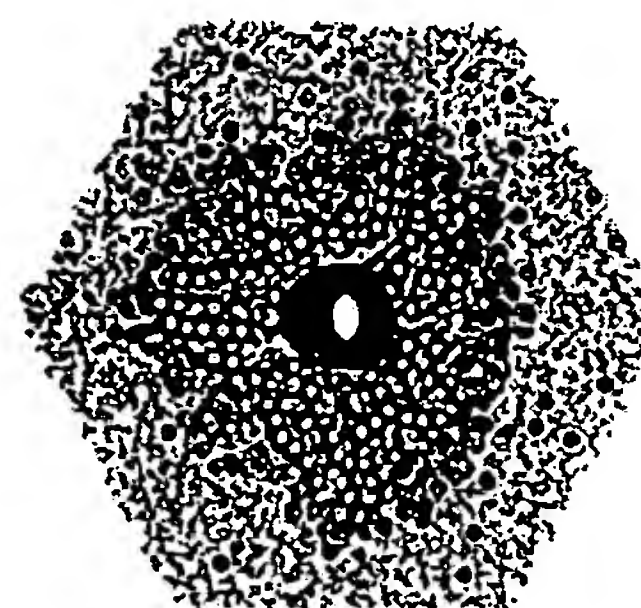
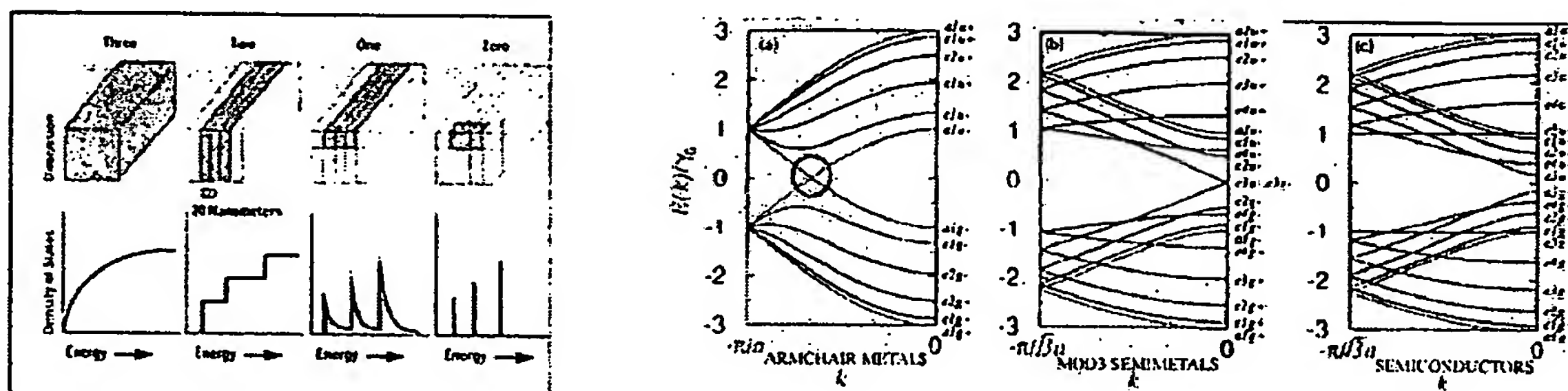


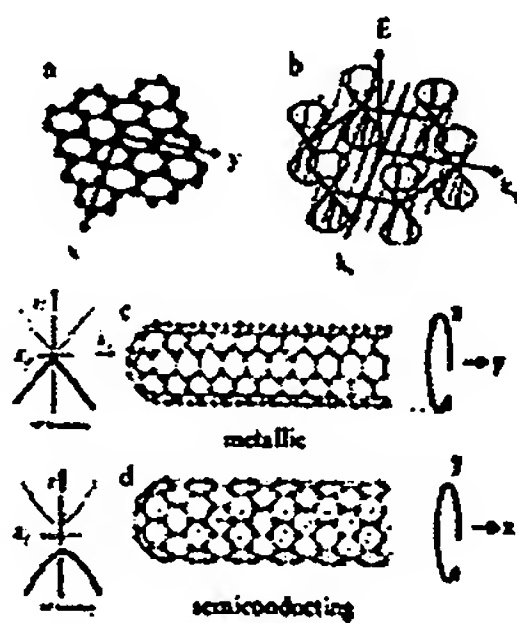
Photo-labile surfactants enable SWNT separations. [15]

**Armchair Quantum Wire.** Recent research efforts on individual Single-Wall Carbon NanoTubes (SWNT) have demonstrated as fact the much-heralded expectation that certain SWNT types have the highest known carrier mobilities and current densities approaching  $10^{10}$  A-cm<sup>-2</sup> [16, 17]. These results, combined with less famous experimental and computational results involving electron-phonon interactions, carrier lifetimes and mean free paths, we can now realize a solid opportunity to develop revolutionary macro-scale electrical components based on SWNT fibers and cable assemblies. Indeed it is reasonable to expect that a proper development and integration of specific-type SWNT, high-transmission contacts and fiber processing technology could yield conductors with over two orders of magnitude improvement over copper in current carrying capacity per unit weight. This approaches the practical range of high temperature superconductor engineering – about 100x the current density of copper – but without cryogenics.

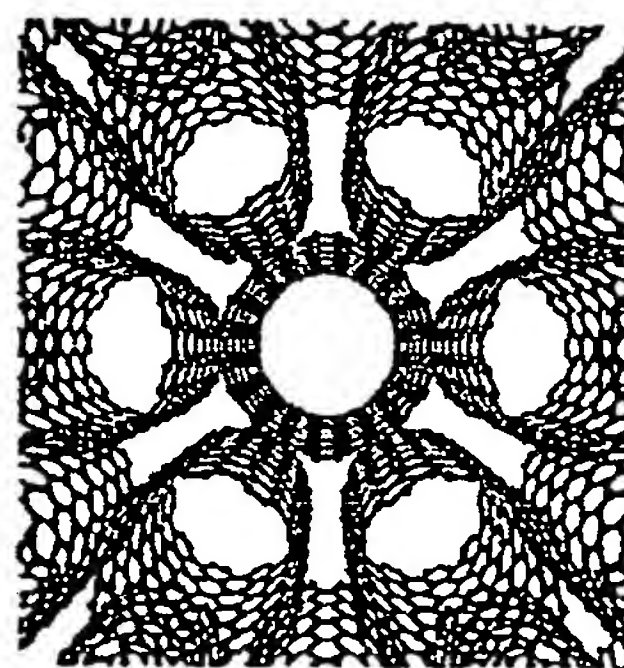
To describe how we will do this and why we are confident of a positive result, we should review the electronic properties of SWNT. Since SWNT are uni-dimensional, their band structures differ from familiar bulk materials in important ways. With decreased dimensionality, energy levels become increasingly quantized, meaning that the number of allowed states for an electron (or phonon...) is reduced (see figure below, left). Calculated band structures for the three generic types of ideal, isolated SWNT are shown below (right) [1].



For bulk conductance, plainly we are interested in the metallic tubes. Semi-metals have a very small band-gap (on the order of kT), and so are conductive at room temperature, but have lower conductivity than true metals, so our interest is focused on the latter – the Armchair tubes – hence the Armchair Quantum Wire.



Local Geometry Defines Electronic Structure



Perspective View of AQW Bundle of (10,10) SWNT

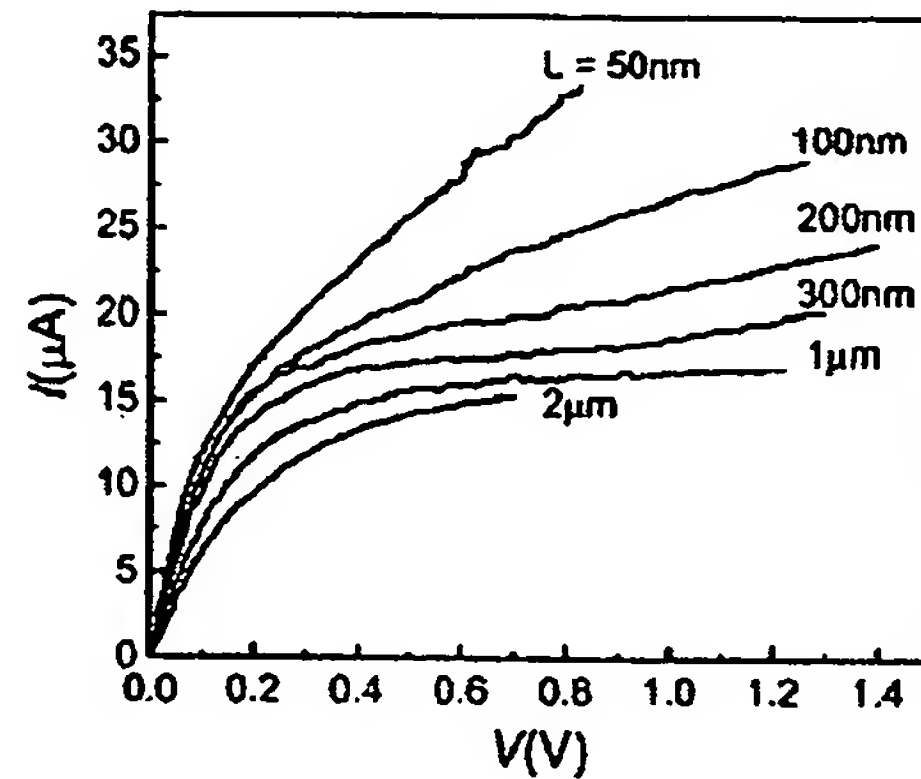
SWNT are uni-dimensional conductors with diameters around one nanometer, they behave as individual quantum wires. Thus, conduction from contact to tube to contact has to be treated as a unified quantum event. Essentially, to get conduction have to match the tube's wave function to those of the contacts – contact transmission becomes important, as well as the number of allowed states or bands, in the conductor. For metallic tubes (of either kind), the resistivity with four sub-bands in the incoherent limit is given by Landauer's equation:

$$R = \left( \frac{h}{4e^2 T} \right) \cdot L_{\text{wire}} \left( \frac{1}{\lambda_e} + \frac{1}{\lambda_{ac}} + \frac{1}{\lambda_{opt}} \right)$$



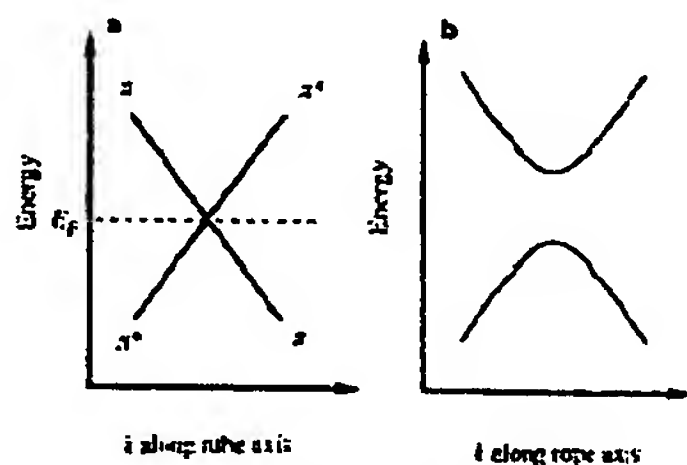
where  $h/4e^2 = 6.5 \text{ k}\Omega$ ,  $T$  is the transmission of the metal contacts to the nanotube,  $L$  the length of the tube, and the  $\lambda$ s the mean free paths for scattering by impurities (elastic scattering), and acoustic and optical phonons (inelastic scattering), respectively. The collection of  $1/\lambda$  terms is manifested as the mean free path of the electron before a back-scattering event. Nominally,  $\lambda_e$  is a few microns (due to impurities/adsorbates),  $\lambda_{ac}$  is long, and  $\lambda_{opt}$  depends on the applied voltage. In a high energy ballistic regime where the energy of the electrons exceeds  $\sim 0.2 \text{ eV}$ , excitation of optical phonons becomes possible, and reduces the mean free path of about 20 nanometers.

Plainly, this is a topic of some interest due to the importance of quantum wire behavior in SWNT device electronics. Short, individual tubes have been studied rather extensively, though by no means exhaustively or perfectly. Key results have been reported by McEuen [16,17], that bear out the basic features of the above prediction. Indeed, with good contacts, a very attractive effective resistance was found in the low field regime –  $4 \text{ K}\Omega / \mu\text{m}$ . This was mediated by interaction with low energy (acoustic) phonons. At high fields, optical phonon interactions become very pronounced and effectively clamp the maximum current through the tube to about  $25 \mu\text{A}$ . The figure at right shows  $i$ - $V$  curves measured at several positions along a given nanotube. This exciting result does not represent the ultimate for SWNT. The exact tube type was not determined (it could have been either armchair or mod3). Substrate interactions, bends and impurities all existed, but could not be eliminated from the result.

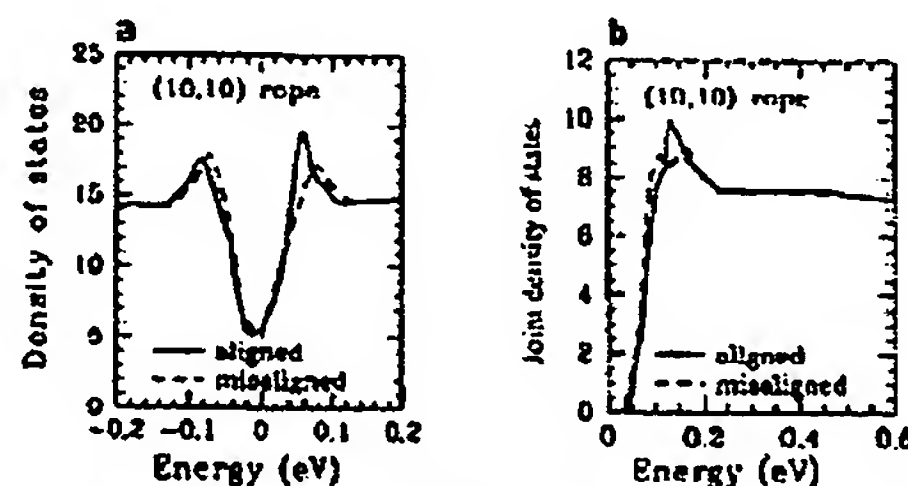


Still, the results bode extremely well for AQW. The inferred mean free path was  $1.6 \mu\text{m}$ . Given the measured diameter of the test article,  $1.8 \text{ nm}$ , the equivalent bulk resistivity of an assembly of such tubes would be about 2.5 times better than copper, with  $\rho \approx 0.7 \mu\Omega\cdot\text{cm}$ . Normalized to the density of the materials (SWNT vs. Cu), the conductivity-weight performance would be about 20 times better than copper.

Our goal is not individual tubes, but vast assemblies of armchair SWNT packed into hexagonal arrays. Comprehensive theory for this situation is lacking. Calculations on representative structures have been performed, however, and the results are intriguing. Louie, Cohen, et al., [19] have published interesting results predicting the appearance of a “micro-gap” in a bundle of (10,10) tubes due to reduced radial symmetry in a given tube’s local environment. Indeed, in some elegant work by Lieber, et al. [20], electron Density of States (DOS) measurements of a metallic tube in a bundle appear to display such a feature.



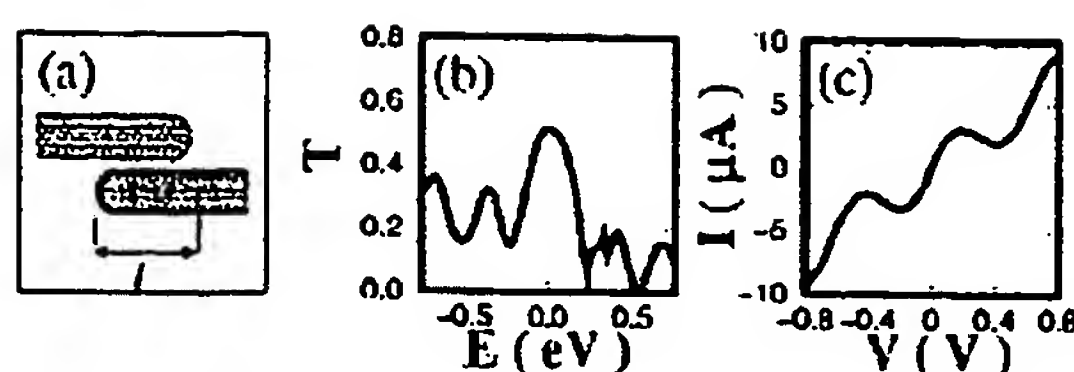
Bundling Could Create A “Micro-Gap” [19]



Calculated Micro-Gap DOS In (10,10) Bundles [19]

What exactly this might mean for a real conductor is not at all clear. A significant reduction in DOS at the Fermi level could reduce conductivity. However, the phonon DOS will undergo similar changes [21, 22, 23], thereby decreasing the ability of acoustic phonons to impede electron flow. These are competing effects that will have to be investigated experimentally.

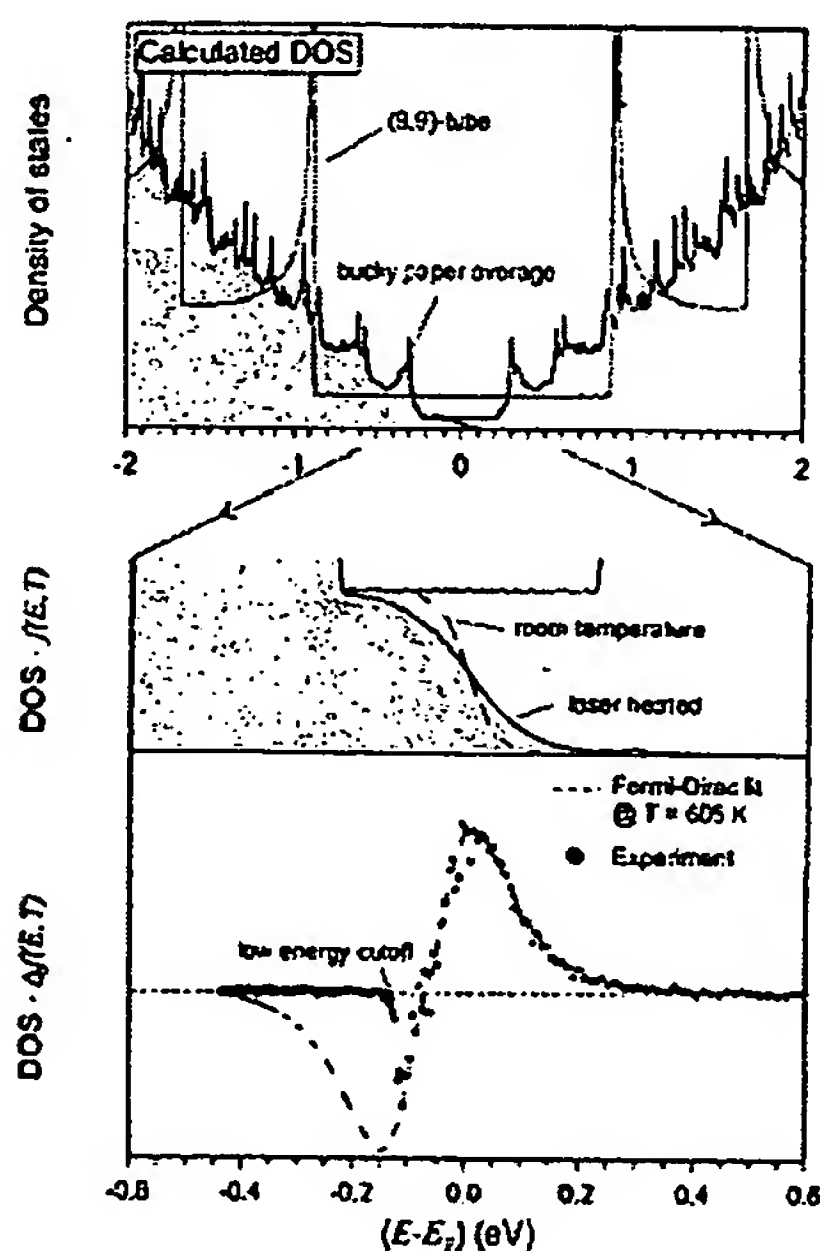
As mentioned in the introduction, maintaining clonal purity in Armchair Quantum Wire will be critical to maintaining high conductivity in bulk assemblies. This will enable us to take advantage of resonant quantum tunneling effects between adjacent tubes of identical type. This effect has been modeled by Buldum and Lu [26].



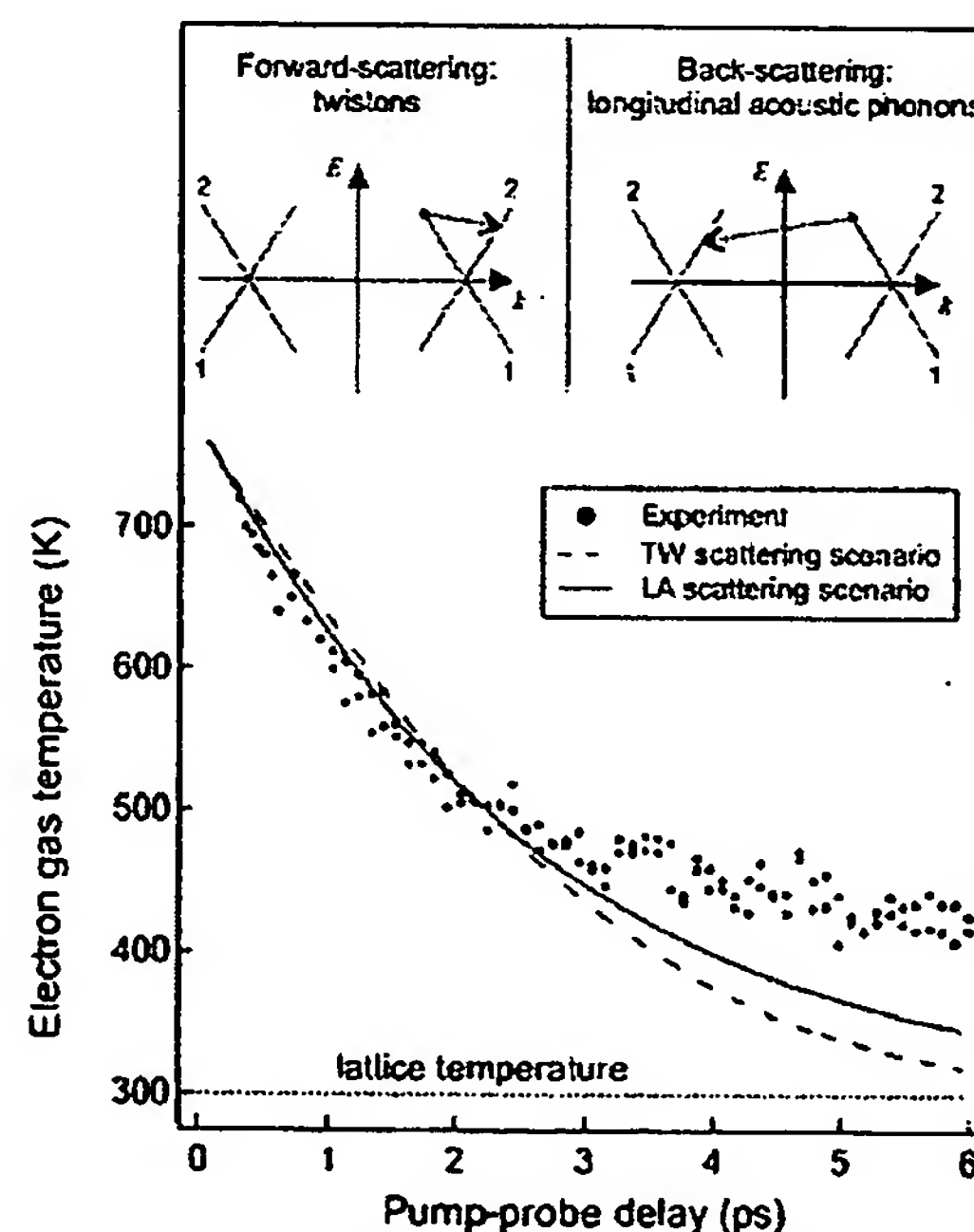
Tube-Tube Resonant Quantum Tunneling Preserves High Conductivity In The ArmChair Quantum Wire [26].

Their key results are shown above, right, and demonstrate that the quantum transmission coefficient (per Landauer) will be better than 0.5 in the energy range of interest, as long as the overlap between adjacent tubes is on the order of 100 nm. This essentially defeats reflection at the ends of tubes of finite length. With basic SWNT elements over 10 microns in length, we would expect the macroscopic resistivity of AQW to be not more than twice that of wire constructed of infinitely long tubes.

In an important report by Hertel, *et al.* [24], many of these issues can be resolved. Using a buckypaper sample produced at Rice, Hertel measured the mean free path of electrons in ropes of mixed SWNT. The ropes in buckypaper are very nearly perfect hexagonal arrays of very high quality SWNT. Thus, the structure is microscopically very similar to our proposed Quantum Wire. Furthermore, the clever nature of the experiment eliminates terminal contact transmission effects, and includes the effects of finite length nanotubes in bundles of macroscopic lengths.



Laser Excitation Pumps SWNT Electron Temperature [24]



TOF Photo-Ionization Probes Electron Cooling Rate [24]

Specifically, Hertel's clever pump-probe experiment perturbs the electron energy distribution (temperature) with one photon, and then measures the temperature as a function of time using a second ionizing photon. The electron's level (temperature) is inferred from the energy of the ejected electron by time-of-flight. Hertel's conclusion is that the electron's mean free path is about 15 microns in this mixture – an order of magnitude greater than McEuen's result using isolated SWNT. Since a) the sample contained only a fraction of metallic SWNT and b) only a fraction of these were Armchairs, and c) the SWNT nanotubes in the sample were only about one micron in length, we might take this as a lower bound on the ultimate performance of Armchair Quantum Wire. Interestingly, the electrons cooled more slowly (*i.e.* had less loss to phonons) than current theory predicts – this may be a manifestation of efficient lateral tube-tube tunneling, per computational predictions [25, 26]. Plainly, such results behoove us to explore and model this arrangement in more detail during the proposed program.

If Quantum Wires perform at least this well on the macro-scale, their basic conductivity would be about 25 times that of copper, and normalized to mass, AQW would provide two orders of magnitude advantage over copper. Additional optimizations may be possible as well. For instance, modeling results by Anantram [27, 28, 29, 30] hint that larger tubes will have more useable sub-bands, and that tunneling contacts may increase transmission factors by a factor of two over the Landauer norm.

There will be, of course, many degrees of freedom that will have to be explored, characterized and controlled in the AQW program to realize the maximum possible performance of SWNT aggregates in large conductors. Chiefly, we will have to master production of specific types of SWNT on large scales, and develop processing methods for forming large almost-perfect arrays without degrading the purity of the material. Additional work will be required on optimizing contact metallization along with optimal SWNT type selection. All of these development activities will need to be supported by an integrated modeling effort, as well. Though challenging, a strong and focused Quantum Wire program should deliver a truly revolutionary product while simultaneously enabling a new class of affordable materials and technologies.

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## Constructive Plan

### Task 1. Cloning Process Development.

Rationale	While the needs for large amounts of pure, type-selected SWNT are clear, current SWNT production technology has several key limitations. Most importantly, combining catalyst formation, nucleation and growth at high temperatures results in high levels of impurities and by-products while complicating reactor design and construction. Current conditions also allow for promiscuous nucleation of multiple SWNT types, though limited control of type distributions has been demonstrated.
Approach	Via 'cloning', we shall rationally separate critical SWNT production steps, especially those of catalyst formation and tube growth. Promiscuous nucleation will be avoided entirely by operating at lower temperatures and using seeds produced from small quantities of class- and type-selected SWNT feedstock. Seeds will be made by physi-chemical cutting of selected SWNT. Several cutting approaches have been preliminarily demonstrated; these will be further explored and the optimal process developed. Key SWNT organic and organo-metallic functionalization chemistries for SWNT are known; routes for attaching pre-formed catalyst particles to cut tubes will be explored and the optimal pathway further developed. Known methods exist for rationally forming nanometer-scale metal and alloy particles under mild conditions; these include self-assembled Keplerates and surfactant-stabilized condensates of metal carbonyls. These methods will be explored and the optimal system developed. Micro-scale separation of specific SWNT are sufficient for the program needs; we shall explore and extend prior efforts based on physical, chemical and electro-dynamic methods to produce a catalog of feedstocks for cloning production. We shall initially demonstrate, characterize and integrate the several process steps using individually observable seeds immobilized on well-defined surfaces. Later stages will involve micro- and bench scale production of type-selected SWNT. Technical results will be transferred continually to Task 3. for scaling and production planning.
Benefits	<ol style="list-style-type: none"><li>1. Process technology for significantly increasing purity of as-grown SWNT.</li><li>2. Process technology for manufacturing single-type selected SWNT.</li><li>3. Process technology for low cost, high-volume SWNT production.</li></ol>
Sub-Tasks	<ol style="list-style-type: none"><li>1. Develop cloning catalyst production to 30-gram levels; prove kilo feasibility.</li><li>2. Develop SWNT cutting to kilo levels; prove ton feasibility.</li><li>3. Develop SWNT functionalization to kilo levels; prove ton feasibility.</li><li>4. Develop attach process to 30-gram levels; prove kilo feasibility.</li><li>5. Develop class-specific SWNT separations to 30-gram level.</li><li>6. Develop type-specific SWNT separations to gram level.</li><li>7. Demonstrate full-cycle cloning on well-defined surfaces.</li><li>8. Develop supported seed methodology to kilo level; prove ton feasibility.</li><li>9. Produce and deliver class- and type-selected seeds to other Tasks.</li><li>10. Model and document technology for transfer to commercial operations.</li></ol>

### Task 2. Ordered Growth & Template Assembly.

Rationale	Current SWNT production technology based upon gas-phase precipitation in a flow-through reactor results in geometrically disordered growth, which reduces yield and throughput. The resulting fluffy bulk complicates reactor design, impedes continuous production and makes post-processing into shaped articles difficult. Growth from dense well-ordered templates is therefore highly desirable for production scaling. Similarly, continuous growth from solid pre-forms, including membranes, plates, fibers and rods will help speed development of several applications.
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**Approach** Ordered substrates will be developed concurrently along two paths – a) performs fabricated from one or more wet-spun SWNT fibers, and b) thin-film templates assembled from SWNT seeds. Well defined catalyst particles and attach chemistries from Task 1 will be employed in this effort. Conceptual feasibility for this approach has been demonstrated using thin-film catalyst layers deposited in high vacuum on cut fiber ends. Larger areas of more complicated geometries will necessitate development of thin film seed templates. Various known phenomena including shear orientation, chemically-directed self-assembly, electrodynamics and electrophoresis will be explored and exploited to develop a general methodology for producing vertically-oriented seed beds. Finally, we shall explore electrostatic and magnetic means for orienting seed-catalyst in the gas phase and dynamically depositing them on the surface of growing SWNT objects, e.g. rods and plates in a medium temperature reactor system.

**Benefits**

1. Improved productivity in flow-through SWNT production reactors.
2. Reduced post-processing and handling required for shaped articles.
3. Enable near-net-shape production of complex SWNT components.
4. Enable tailored SWNT membrane and arrays power & quantum devices.

**Sub-Tasks**

1. Develop fabrication and pre-prep methods for fiber-based substrates to 1 cm<sup>2</sup>.
2. Develop catalyst attach and docking methods for substrates up to 1 cm<sup>2</sup>.
3. Develop methods for assembling arrays of seeds on substrates up to cm<sup>2</sup>.
4. Develop methods for depositing oriented seeds on articles in-situ.
5. Demonstrate continuous growth over 1 cm<sup>2</sup>; prove feasibility for 1 cm x 1 meter.
6. Produce, characterize and deliver test articles to Partners and other Projects.
5. Model and document process and reactor technology for commercial transfer.

### Task 3. SWNT Production & Scaling.

**Rationale** Various complexities and inefficiencies of current growth technology limits production volumes, necessitates laborious purification and results in high costs. Within current approaches, recent results indicate that some of these issues can be partially ameliorated. New growth and production approaches from Tasks 1 and 2, can be implemented incrementally. Current and planned SWNT research and development requires a continuous flow of working material – at ever increasing volumes and with continually more stringent specificity.

**Approach** Our approach to development needs and future capacity is to maintain and incrementally improve current production technology, while simultaneously developing new reactors that exploit advances gained concurrently in Tasks 1 and 2. In-house efforts will extend through bench and laboratory-scale reactor modeling, design, construction, operation and evaluation. Supporting operations for material characterization and purification, if needed, will be developed concurrently. Bulk and specialty material will be delivered to other Program Partners as needed and as available. Technical results of the program will be codified for subsequent commercialization and production.

**Benefits**

1. Continuous and increasing supply of SWNT at monotonically decreasing cost.
2. High-purity SWNT production (10x to 100x better than current).
3. Type-Selected SWNT for application development.
4. Scalable low-cost SWNT production technology for commercialization.

**Sub-Tasks**

1. SWNT production, purification, characterization & delivery.
2. HiPco process variation and improvement.
3. Liquid/gas seed injection reactor development.
4. Continuous product extraction for gas-phase reactors.
4. Fixed-bed reactor for supported seed growth development.
5. Fluidized-bed continuous reactor for supported seed growth development.
6. Process & reactor modeling and scale-up planning.



#### Task 4. Armchair Quantum Wire.

Rationale	Experimental results on individual nanotubes indicate current carrying capacities vastly superior to copper. Modeling results indicate that type-matched tubes of finite lengths over 100 nm will enjoy efficient lateral quantum tunneling. Thus, well axially connected quasi-crystalline fibers and cables of same-type metallic SWNT should exhibit extremely high power carrying capacity, along with high mechanical strength and low TCE.
Approach	Using first mixed-metallic, then type-optimized SWNT, CNL staff will initially fabricate small-gage conductors using previously demonstrated methodology based on spinning quasi liquid crystalline SWNT/super-acid mixtures. Post-processing techniques will be evaluated and developed for maximizing alignment, crystallinity and connectivity. Test articles will be fully characterized and compared to expectations developed from computational modeling and predictions. Alternative/enhanced coagulation/crystallization methods will be explored, including electrodynamic crystallization, net-shape continuous growth and fiber-bundle re-crystallization. The most promising of these will be further developed for production of higher-gage quantum cables.
Benefits	<ol style="list-style-type: none"><li>1. Improved strength &amp; weight factors in aerospace signaling systems</li><li>2. Reduced weight in power busses in aerospace and man-portable systems</li><li>3. Reduced weight, size &amp; cost in propulsion motors &amp; motor/generator sets.</li><li>4. Higher reliability, strength &amp; power density for electric grid cabling with zero sag.</li></ol>
Sub-Tasks	<ol style="list-style-type: none"><li>1. Super-Acid Spinning for SWNT Quantum Conductors (AQW).</li><li>2. Computational Modeling of SWNT Conductor Systems.</li><li>3. Characterization &amp; Metrology of SWNT Conductor Systems.</li><li>4. Electrodynamic Consolidation for Quantum Conductors.</li><li>5. Net-Shape Continuous Fiber/Cable Growth.</li><li>6. Fiber Bundle Re-Forming/Re-Crystallization.</li><li>7. Post-Processing Connectivity Optimization.</li><li>8. Microelectronic Interconnect Applications Research.</li><li>9. Aerospace Vehicle Signal &amp; Power Applications Research.</li><li>10. Motor/Generator Applications Research.</li><li>11. Quantum Wire Production and Scaling Plans.</li></ol>

**WHAT IS CLAIMED IS:**

1. All inventions as described substantially herein.

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Suggested Group Art Unit::	
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